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Multi-Agency Radiological Laboratory Analytical Protocols Manual

Volume I: Chapters 1 – 9 and Appendices A – E

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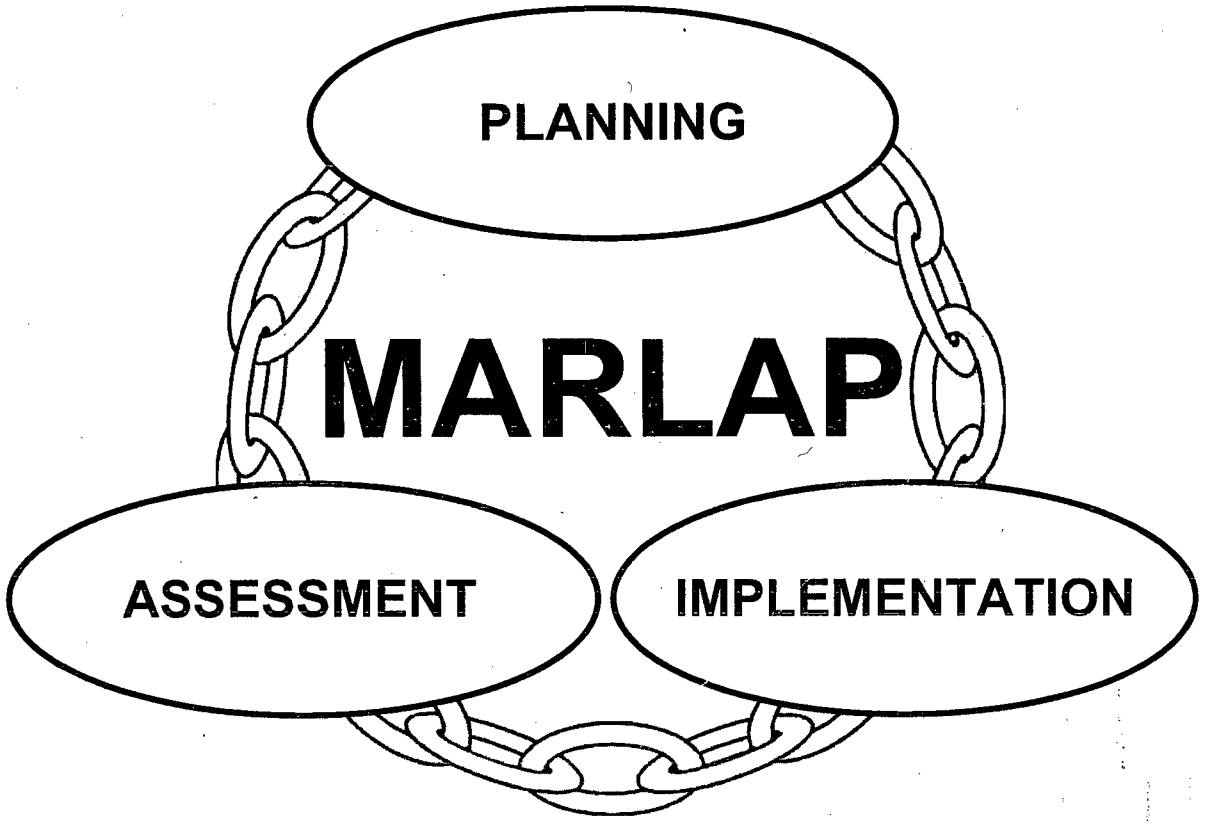

FDA USGS NIST

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ABSTRACT

The Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) manual provides guidance for the planning, implementation, and assessment of projects that require the laboratory analysis of radionuclides. MARLAP's basic goal is to provide guidance for project planners, managers, and laboratory personnel to ensure that radioanalytical laboratory data will meet a project's or program's data requirements. To attain this goal, the manual offers a framework for national consistency in the form of a performance-based approach for meeting data requirements that is scientifically rigorous and flexible enough to be applied to a diversity of projects and programs. The guidance in MARLAP is designed to help ensure the generation of radioanalytical data of known quality, appropriate for its intended use. Examples of data collection activities that MARLAP supports include site characterization, site cleanup and compliance demonstration, decommissioning of nuclear facilities, emergency response, remedial and removal actions, effluent monitoring of licensed facilities, environmental site monitoring, background studies, and waste management activities.

MARLAP is organized into two parts. Part I, intended primarily for project planners and managers, provides the basic framework of the directed planning process as it applies to projects requiring radioanalytical data for decision making. The nine chapters in Part I offer recommendations and guidance on project planning, key issues to be considered during the development of analytical protocol specifications, developing measurement quality objectives, project planning documents and their significance, obtaining laboratory services, selecting and applying analytical methods, evaluating methods and laboratories, verifying and validating radiochemical data, and assessing data quality. Part II is intended primarily for laboratory personnel. Its eleven chapters provide detailed guidance on field sampling issues that affect laboratory measurements, sample receipt and tracking, sample preparation in the laboratory, sample dissolution, chemical separation techniques, instrumentation for measuring radionuclides, data acquisition, reduction, and reporting, waste management, laboratory quality control, measurement uncertainty, and detection and quantification capability. Seven appendices provide complementary information and additional details on specific topics.

MARLAP was developed by a workgroup that included representatives from the U.S. Environmental Protection Agency (EPA), Department of Energy (DOE), Department of Defense (DOD), Department of Homeland Security (DHS), Nuclear Regulatory Commission (NRC), National Institute of Standards and Technology (NIST), U.S. Geological Survey (USGS), and Food and Drug Administration (FDA), and from the Commonwealth of Kentucky and the State of California.

CONTENTS

Page

Page

Page

Page

Volume II

Page

Page

Page

Page

Page

Volume III

Page

Page

Page

Appendices – Volume I

Page

Page

Page

Appendices – Volume II

Appendices – Volume III

Page

List of Figures

Volume II

Page

Volume III

Page

Page

Page

List of Tables

Volume II

Page

Volume III

Page

Page

1 INTRODUCTION TO MARLAP

1.1 Overview

Each year, hundreds of millions of dollars are spent on projects and programs that rely, to varying degrees, on radioanalytical data for decisionmaking. These decisions often have a significant impact on human health and the environment. Of critical importance to informed decisionmaking are data of known quality, appropriate for their intended use. Making incorrect decisions due to data inadequacies, such as failing to remediate a radioactively contaminated site properly, necessitates the expenditure of additional resources, causes delays in project completions and, depending on the nature of the project, can result in the loss of public trust and confidence. The Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual addresses the need for a nationally consistent approach to producing radioanalytical laboratory data that meet a project's or program's data requirements. MARLAP provides guidance for the planning, implementation, and assessment phases of those projects that require the laboratory analysis of radionuclides. The guidance provided by MARLAP is both scientifically rigorous and flexible enough to be applied to a diversity of projects and programs. This guidance is intended for project planners, managers, and laboratory personnel.

MARLAP is divided into two main parts. Part I is primarily for project planners and managers and provides guidance on project planning with emphasis on analytical planning issues and analytical data requirements. Part I also provides guidance on preparing project plan documents and radioanalytical statements of work (SOWs), obtaining and evaluating radioanalytical laboratory services, data validation, and data quality assessment. Part I of MARLAP covers the entire life of a project that requires the laboratory analysis of radionuclides from the initial project planning phase to the assessment phase.

Part II of MARLAP is primarily for laboratory personnel and provides guidance in the relevant areas of radioanalytical laboratory work. Part II offers information on the laboratory analysis of radionuclides. The chapters in Part II cover the range of activities performed at radioanalytical laboratories, including sample preservation, shipping and handling, sample preparation, sample dissolution, separation techniques, instrument measurements, data reduction, quality control, statistics, and waste management. Part II is not a compilation of analytical procedures but rather is intended to provide information on many of the radioanalytical options available to laboratories and discuss the advantages and disadvantages of each.

MARLAP was developed collaboratively by the following federal agencies: the Environmental Protection Agency (EPA), the Department of Energy (DOE), the Department of Homeland

Contents

Security (DHS), the Nuclear Regulatory Commission (NRC), the Department of Defense (DOD), the National Institute of Standards and Technology (NIST), the United States Geological Survey (USGS), and the Food and Drug Administration (FDA). State participation in the development of MARLAP involved contributions from representatives from the Commonwealth of Kentucky and the State of California.

1.2 Purpose of the Manual

MARLAP's basic goal is to provide guidance for project planners, managers, and laboratory personnel to ensure that radioanalytical laboratory data will meet a project's or program's data requirements and needs. To attain this goal, MARLAP provides the necessary framework for national consistency in radioanalytical work in the form of a performance-based approach for meeting a project's data requirements. In general terms, a performance-based approach to laboratory analytical work involves clearly defining the analytical data needs and requirements of a project in terms of measurable goals during the planning phase of a project. These project-specific analytical data needs and requirements then serve as measurement performance criteria for decisions as to exactly how the laboratory analysis will be conducted during the implementation phase of a project. They are used subsequently as criteria for evaluating analytical data during the assessment phase. The manual focuses on activities performed at radioanalytical laboratories as well as on activities and issues that direct, affect, or can be used to evaluate activities performed at radioanalytical laboratories.

Specific objectives of MARLAP include:

- Promoting a directed planning process for projects involving individuals from relevant disciplines including radiochemistry;
- Highlighting common radioanalytical planning issues;
- Providing a framework and information resource for using a performance-based approach for planning and conducting radioanalytical work;
- Providing guidance on linking project planning, implementation, and assessment;
- Providing guidance on obtaining and evaluating radioanalytical laboratory services;
- Providing guidance for evaluating radioanalytical laboratory data, i.e., data verification, data validation, and data quality assessment;
- Promoting high quality radioanalytical laboratory work; and

- Making collective knowledge and experience in radioanalytical work widely available.

1.3 Use and Scope of the Manual

The guidance contained in MARLAP is for both governmental and private sectors. Users of MARLAP include project planners, project managers, laboratory personnel, regulators, auditors, inspectors, data evaluators, decisionmakers, and other end users of radioanalytical laboratory data.

Because MARLAP uses a performance-based approach to laboratory measurements, the guidance contained in the manual is applicable to a wide range of projects and activities that require radioanalytical laboratory measurements. Examples of data collection activities that MARLAP supports include:

- Site characterization activities;
- Site cleanup and compliance demonstration activities;
- License termination activities;
- Decommissioning of nuclear facilities;
- Remedial and removal actions;
- Effluent monitoring of licensed facilities;
- Emergency response activities;
- Environmental site monitoring;
- Background studies;
- Routine ambient monitoring; and
- Waste management activities.

MARLAP and the *Multi-Agency Radiation Survey and Site Investigation Manual* (MARSSIM, 2000) are complementary guidance documents in support of cleanup and decommissioning activities. MARSSIM provides guidance on how to plan and carry out a study to demonstrate that a site meets appropriate release criteria. It describes a methodology for planning, conducting, evaluating, and documenting environmental radiation surveys conducted to demonstrate compliance with cleanup criteria. MARLAP provides guidance and a framework for both project planners and laboratory personnel to ensure that radioanalytical data will meet the needs and requirements of cleanup and decommissioning activities.

While MARLAP supports a wide range of projects, some topics are not specifically discussed in the manual. These include high-level waste, mixed waste, and medical applications involving radionuclides. While they are not specifically addressed, much of MARLAP's guidance may be applicable in these areas. Although the focus of the manual is to provide guidance for those projects that require the laboratory analysis of radionuclides, much of the guidance on the planning and assessment phases can be applied wherever the measurement process is conducted,

for example, in the field. In addition, MARLAP does not provide specific guidance on sampling design issues, sample collection, field measurements, or laboratory health and safety practices. However, a brief discussion of some aspects of these activities has been included in the manual because of the effect these activities often have on the laboratory analytical process.

1.4 Key MARLAP Concepts and Terminology

Some of the terms used in MARLAP were developed for the purpose of this manual, while others are commonly used terms that have been adopted by MARLAP. Where possible, every effort has been made to use terms and definitions from consensus-based organizations (e.g., International Organization for Standardization [ISO], American National Standards Institute [ANSI], American Society for Testing and Materials [ASTM], International Union of Pure and Applied Chemistry [IUPAC]).

The following sections are intended to familiarize the reader with the key terms and concepts used in MARLAP. In general, each term or concept is discussed individually in each section without emphasizing how these terms and concepts are linked. Section 1.5 ties these terms and concepts together to provide an overview of the MARLAP process.

DATA LIFE CYCLE		
PROCESS		PROCESS OUTPUTS
Planning	Directed Planning Process	Development of Data Quality Objectives and Measurement Quality Objectives (Including Optimized Sampling and Analytical Design)
	Plan Documents	Project Plan Documents Including Quality Assurance Project Plan (QAPP); Work Plan or Sampling and Analysis Plan (SAP); Data Validation Plan; Data Quality Assessment Plan
	Contracting Services	Statement of Work (SOW) and Other Contractual Documents
Implementation	Sampling	Laboratory Samples
	Analysis	Laboratory Analysis (Including Quality Control [QC] Samples) Complete Data Package
Assessment	Verification	Verified Data Data Verification Report
	Validation	Validated Data Data Validation Report
	Data Quality Assessment	Assessment Report
Data of Known Quality Appropriate for the Intended Use		

FIGURE 1.1 — The data life cycle

1.4.1 Data Life Cycle

The data life cycle (EPA, 2000) approach provides a structured means of considering the major phases of projects that involve data collection activities (Figure 1.1). The three phases of the data life cycle are *planning*, *implementation*, and *assessment.* Although the diagram represents the data life cycle in a linear fashion, it is important to note that the actual process is an iterative one, with feedback loops. MARLAP provides information on all three phases for two major types of activities: those performed at radioanalytical laboratories and

those that direct, affect, or evaluate activities performed at radioanalytical laboratories (such as project planning, development of plan documents, data verification and data validation).

One of MARLAP's specific objectives is to emphasize the importance of establishing the proper linkages among the three phases of the data life cycle. This results in an integrated and iterative process that translates the expectations and requirements of data users into measurement performance criteria for data suppliers. The integration of the three phases of the data life cycle is critical to ensuring that the analytical data requirements (defined during the planning phase) can serve as measurement performance criteria during the implementation phase and subsequently as data evaluation criteria during the assessment phase.

Without the proper linkages and integration of the three phases, there is a significant likelihood that the analytical data will not meet a project's data requirements. The data may be evaluated using criteria that have little relation to their intended use. Therefore, failure to integrate and adequately link the three phases of the data life cycle increases the likelihood of project cost escalation or project failure.

1.4.2 Directed Planning Process

MARLAP recommends the use of a directed or systematic planning process. A directed planning process is an approach for setting well-defined, achievable objectives and developing a cost-effective, technically sound sampling and analysis design that balances the data user's tolerance for uncertainty in the decision process with the resources available for obtaining data to support a decision. While MARLAP recommends and promotes the use of a directed planning process, it does not recommend or endorse any particular directed planning process. However, MARLAP employs many of the terms and concepts associated with the data quality objective (DQO) process (ASTM D5792; EPA, 2000). This was done to ensure consistent terminology throughout the manual, and also because many of the terms and concepts of this process are familiar to those engaged in environmental data collection activities.

1.4.3 Performance-Based Approach

MARLAP provides the necessary guidance for using a performance-based approach to meet a project's analytical data requirements. In a performance-based approach, the project-specific analytical data requirements that are determined during directed planning serve as measurement performance criteria for analytical selections and decisions. The project-specific analytical data requirements also are used for the initial, ongoing, and final evaluation of the laboratory's performance and the laboratory's data. MARLAP provides guidance for using a performance-based approach for all three phases of the data life cycle for those projects that require radioanalytical laboratory data. This involves not only using a performance-based approach for selecting an analytical protocol, but also using a performance-based approach for other project

activities, such as developing acceptance criteria for laboratory quality control samples, laboratory evaluations, data verification, data validation, and data quality assessment.

There are three major steps associated with a performance-based approach. The first is clearly and accurately defining the analytical data requirements for the project. This process is discussed in more detail in Section 1.4.9 of this chapter. The second step uses an organized, interactive process to select or develop analytical protocols to meet the specified analytical data requirements and to demonstrate the protocols' abilities to meet the analytical data requirements (Section 1.4.10). The third major step uses the analytical data requirements as measurement performance criteria for the ongoing and final evaluation of the laboratory data, including data verification, data validation, and data quality assessment (Section 1.4.11). Within the constraints of other factors, such as cost, a performance-based approach allows for the use of any analytical protocol that meets the project's analytical data requirements. For all relevant project activities, the common theme of a performance-based approach is the use of project-specific analytical data requirements that are developed during project planning and serve as measurement performance criteria for selections, evaluations, and decisionmaking.

1.4.4 Analytical Process

Most environmental data collection efforts center around two major processes: the sampling process and the analytical process. MARLAP does not provide guidance on the sampling process, except for brief discussions of certain activities that often affect the analytical process (field processing, preservation, etc.). The analytical (or measurement) process is a general term used by MARLAP to refer to a compilation of activities starting from the time a sample is collected and ending with the reporting of data. Figure 1.2 illustrates the major components of an analytical process. A particular analytical process for a project may not include all of the activities listed. For example, if a project involves the analysis of

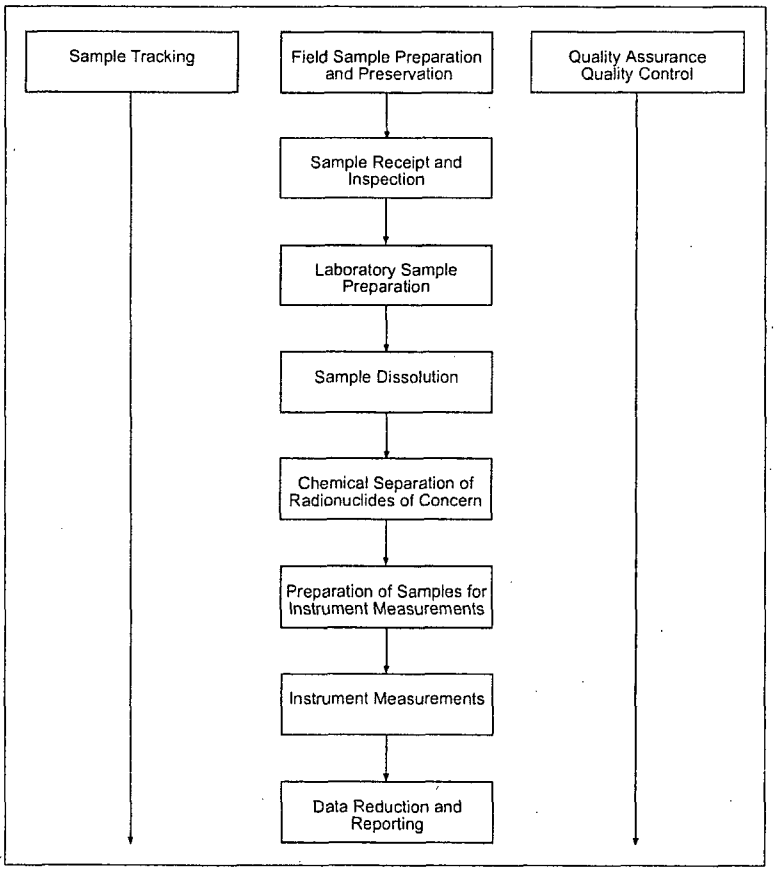

FIGURE 1.2 — Typical components of an analytical process

tritium in drinking water, then the analytical process for the project will not include sample dissolution and the chemical separation of the radionuclide of concern. It is important to identify the relevant activities of the analytical process for a particular project early in the planning phase. Once the activities have been identified, the analytical requirements of the activities can be established, which will ultimately lead to defining how the activities will be accomplished through the selection or development of written procedures.

1.4.5 Analytical Protocol

MARLAP uses the term "analytical protocol" to refer to a compilation of specific procedures and methods that are performed in succession for a particular analytical process. For example, a protocol for the analysis of drinking water samples for tritium would be comprised of the set of procedures that describe the relevant activities, such as sample tracking, quality control, field sample preparation and preservation, sample receipt and inspection, laboratory sample preparation (if necessary), preparing the samples for counting, counting the samples, and data reduction and reporting. A written procedure may cover one or more of the activities, but it is unlikely that a single procedure will cover all of the activities of a given analytical process. With a performance-based approach, there may be a number of alternative protocols that might be appropriate for a particular analytical process. Selecting or developing an analytical protocol requires knowledge of the particular analytical process, as well as an understanding of the analytical data requirements developed during the project planning phase.

1.4.6 Analytical Method

A major component of an analytical protocol is the *analytical method,* which normally includes written instructions for sample digestion, chemical separation (if required), and counting. It is recognized that in many instances the analytical method may cover many of the activities of a particular analytical process. Therefore attention is naturally focused on the selection or development of an analytical method. However, many analytical methods do not address activities such as field preparation and preservation, certain aspects of laboratory preparation, laboratory subsampling, etc., which are often important activities within an analytical process. The analytical protocol is generally more inclusive of the activities that make up the analytical process than the analytical method.

1.4.7 Uncertainty and Error

An important aspect of sampling and measurement is uncertainty. The term "uncertainty" has different shades of meaning in different contexts, but generally the word refers to a lack of complete knowledge about something of interest. In the context of metrology (the science of measurement), the more specific term "measurement uncertainty" often will be used. "Uncertainty (of measurement)" is defined in the *Guide to the Expression of Uncertainty in Measurement* (ISO 1995—"GUM") as a "parameter, associated with the result of a measurement, that charac-

terizes the dispersion of values that could reasonably be attributed to the measurand." The "measurand" is the quantity being measured. MARLAP recommends the terminology and methods of GUM for describing, evaluating, and reporting measurement uncertainty. The uncertainty of a measured value is typically expressed as an estimated standard deviation, called a "standard uncertainty" (or "one-sigma uncertainty"). The standard uncertainty of a calculated result usually is obtained by propagating the standard uncertainties of a number of other measured values, and in this case, the standard uncertainty is called a "combined standard uncertainty." The combined standard uncertainty may be multiplied by a specified factor called a "coverage factor" (e.g., 2 or 3) to obtain an "expanded uncertainty" (a "two-sigma" or "three-sigma" uncertainty), which describes an interval about the result that can be expected to contain the true value with a specified high probability. MARLAP recommends that either the combined standard uncertainty or an expanded uncertainty be reported with every result. Chapter 19 discusses the terminology, notation, and methods of GUM in more detail and provides guidance for applying the concepts to radioanalytical measurements.

While measurement uncertainty is a parameter associated with an individual result and is calculated after a measurement is performed, MARLAP uses the term "method uncertainty" to refer to the predicted uncertainty of a measured value that likely would result from the analysis of a sample at a specified analyte concentration. Method uncertainty is a method performance characteristic much like the detection capability of a method. Reasonable values for both characteristics can be predicted for a particular method based on typical values for certain parameters and on information and assumptions about the samples to be analyzed. These predicted values can be used in the method selection process to identify the most appropriate method based on a project's data requirements. Chapter 3 provides MARLAP's recommendations for deriving analytical protocol selection criteria based on the required method uncertainty and other analytical requirements.

When a decisionmaker bases a decision on the results of measurements, the measurement uncertainties affect the probability of making a wrong decision. When sampling is involved, sampling statistics also contribute to the probability of a wrong decision. Because decision errors are possible, there is uncertainty in the decisionmaking process. MARLAP uses the terms "decision uncertainty" or "uncertainty of the decision" to refer to this type of uncertainty. Decision uncertainty is usually expressed as the estimated probability of a decision error under specified assumptions. Appendix B discusses decision uncertainty further in the context of the DQO process.

A concept that should not be confused with uncertainty is error. In general, error refers to something that deviates from what is correct, right or true. In terms of measurements such as laboratory analyses, the difference between the measured result and the actual value of the measurand is the error of the measurement. Because the actual value of the measurand is generally not known, the measurement error cannot be determined. Therefore, the error of a measurement is primarily a theoretical concept with little practical use. However, the

measurement uncertainty, which provides an estimated bound for the likely size of the measurement error, is very useful and plays a key role in MARLAP's performance-based approach.

1.4.8 Precision, Bias, and Accuracy

Analytical data requirements often have been described in terms of precision and bias. Precision is usually expressed as a standard deviation, which measures the dispersion of measured values about their mean. It is sometimes more natural to speak of "imprecision," because larger values of the standard deviation indicate less precision. MARLAP considers bias to be a persistent difference between the measured result and the true value of the quantity being measured, which does not vary if the measurement is repeated. If the measurement process is in statistical control, then precision may be improved by averaging the results of many independent measurements of the same quantity. Bias is unaffected by averaging (see Section 6.5.5.7).

A bias in a data set may be caused by measurement errors that occur in steps of the measurement process that are not repeated, such as the determination of a half-life. Imprecision may be caused by measurement errors in steps that are repeated many times, such as weighing, pipetting, and radiation counting. However, distinguishing between bias and precision is complicated by the fact that some steps in the process, such as instrument calibration or tracer preparation, are repeated at frequencies less than those of other steps, and the measurement errors in seldom repeated steps may affect large blocks of data. Consequently, measurement errors that produce apparent biases in small data sets might adversely affect precision in larger data sets.

Because the same type of measurement error may produce either bias or precision, depending on one's point of view, the concept of measurement uncertainty, described in Section 1.4.7, treats all types of measurement error alike and combines estimates of their magnitudes into a single numerical parameter (i.e., combined standard uncertainty). The concepts of precision and bias are useful in context when a measurement process or a data set consisting of many measurement results is considered. When one considers only a single measurement result, the concept of measurement uncertainty tends to be more useful than the concepts of precision and bias. Therefore, it is probably best to consider precision and bias to be characteristics of the measurement process or of the data set, and to consider measurement uncertainty to be an aspect of each individual result.

Quality control samples are analyzed for the purpose of assessing precision and bias. Spiked samples and method blanks are typically used to assess bias, and duplicates are used to assess precision. Because a single measurement of a spike or blank cannot in principle distinguish between precision and bias, a reliable estimate of bias requires a data set that includes many such measurements.

Different authors have given the word *accuracy* different technical definitions, expressed in terms of bias and precision. MARLAP avoids all of these technical definitions and uses the term "accuracy" in its common, ordinary sense, which is consistent with its definition in the *International Vocabulary of Basic and General Terms in Metrology* (ISO, 1993). In MARLAP's terminology, the result of a measurement is "accurate" if it is close to the true value of the quantity being measured. Inaccurate results may be caused either by bias or precision in the measurement process.

While it is recognized that the terms bias, precision, and accuracy are commonly used in data collection activities, these terms are used somewhat sparingly in this manual. MARLAP emphasizes and provides guidance in the use of measurement uncertainty as a means of establishing analytical data requirements and in the evaluation of single measurement results.

1.4.9 Performance Objectives: Data Quality Objectives and Measurement Quality Objectives

One of the outputs of a directed planning process is DQOs for a project or program. DQOs are qualitative and quantitative statements that clarify the study objectives, define the most appropriate type of data to collect, determine the most appropriate conditions from which to collect the data, and specify tolerable limits on decision error rates (ASTM D5792; EPA, 2000). DQOs apply to all data collection activities associated with a project or program, including sampling and analysis. In particular, DQOs should encompass the "total uncertainty" resulting from all data collection activities, including analytical and sampling activities.

From an analytical perspective, a process of developing the analytical data requirements from the DQOs of a project is essential. These analytical data requirements serve as measurement performance criteria or objectives of the analytical process. MARLAP refers to these performance objectives as "measurement quality objectives" (MQOs). The MARLAP Manual provides guidance on developing the MQOs from the overall project DQOs (Chapter 3). MQOs can be viewed as the analytical portion of the DQOs and are therefore project-specific. MARLAP provides guidance on developing MQOs during project planning for select method performance characteristics, such as method uncertainty at a specified concentration; detection capability; quantification capability; specificity, or the capability of the method to measure the analyte of concern in the presence of interferences; range; ruggedness, etc. An MQO is a statement of a performance objective or requirement for a particular method performance characteristic. Like DQOs, MQOs can be quantitative and qualitative statements. An example of a quantitative MQO would be a statement of a required method uncertainty at a specified radionuclide concentration, such as the action level—i.e., "a method uncertainty of 3.7 Bq/kg (0.10 pCi/g) or less is required at the action level of 37 Bq/kg (1.0 pCi/g)." An example of a qualitative MQO would be a statement of the required specificity of the analytical protocol—the ability to analyze for the radionuclide of concern given the presence of interferences—i.e., "the protocol must be able to quantify the amount of ^{226}Ra present given high levels of ^{235}U in the samples."

The MQOs serve as measurement performance criteria for the selection or development of analytical protocols and for the initial evaluation of the analytical protocols. Once the analytical protocols have been selected and evaluated, the MQOs serve as criteria for the ongoing and final evaluation of the laboratory data, including data verification, data validation, and data quality assessment. In a performance-based approach, analytical protocols are either selected or rejected for a particular project, to a large measure, based on their ability or inability to achieve the stated MQOs. Once selected, the performance of the analytical protocols is evaluated using the project-specific MQOs.

1.4.10 Analytical Protocol Specifications

MARLAP uses the term "analytical protocol specifications" (APSs) to refer to the output of a directed planning process that contains the project's analytical data requirements in an organized, concise form. In general, there will be an APS developed for each analysis type. These specifications serve as the basis for the evaluation and selection of the analytical protocols that will be used for a particular project. In accordance with a performance-based approach, the APSs contain only the minimum level of specificity required to meet the project's analytical data requirements without dictating exactly how the requirements are to be met. At a minimum, the APSs should indicate the analyte of interest, the matrix of concern, the type and frequency of quality control (QC) samples, and provide the required MQOs and any specific analytical process requirements, such as chain-of-custody for sample tracking. In most instances, a particular APS document would be a one-page form (see Chapter 3, Figure 3.2). Depending on the particular project, a number of specific analytical process requirements may be included. For example, if project or process knowledge indicates that the radionuclide of interest exists in a refractory form, then the APSs may require a fusion step for sample digestion.

Within the constraints of other factors, such as cost, MARLAP's performance-based approach allows the use of any analytical protocol that meets the requirements in the APSs. The APSs—in particular the MQOs—are used to select and evaluate the analytical protocols. Once the analytical protocols have been selected and evaluated, the APSs then serve as criteria for the ongoing and final evaluation of the laboratory data, including data verification, data validation, and data quality assessment.

1.4.11 The Assessment Phase

The MARLAP Manual provides guidance for the assessment phases for those projects that require the laboratory analysis of radionuclides. The guidance on the assessment phase of projects focuses on three major activities: data verification, data validation, and data quality assessment.

Data verification assures that laboratory conditions and operations were compliant with the statement of work and any appropriate project plan documents (e.g., Quality Assurance Project

Plan), which may reference laboratory documents such as laboratory standard operating procedures. Verification compares the material delivered by the laboratory to these requirements (compliance) and checks for consistency and comparability of the data throughout the data package, correctness of calculations, and completeness of the results to ensure that all necessary documentation is available. The verification process usually produces a report identifying which requirements are not met. The verification report may be used to determine payment for laboratory services and to identify problems that should be investigated during data validation. Verification works iteratively and interactively with the generator (i.e., laboratory) to assure receipt of all available, necessary data. Although the verification process identifies specific problems, the primary function should be to apply appropriate feedback resulting in corrective action improving the analytical services before the work is completed.

Validation addresses the reliability of the data. The validation process begins with a review of the verification report and laboratory data package to screen the areas of strength and weakness of the data set. The validator evaluates the data to determine the presence or absence of an analyte and the uncertainty of the measurement process for contaminants of concern. During validation, the technical reliability and the degree of confidence in reported analytical data are considered. Validation "flags" (i.e., qualifiers) are applied to data that do not meet the acceptance criteria established to assure data meet the needs of the project. The product of the validation process is a validation report noting all data sufficiently inconsistent with the validation acceptance criteria in the expert opinion of the validator. The appropriate data validation tests should be established during the project planning phase.

Data quality assessment (DQA), the third and final step of the assessment phase, is defined as the "scientific and statistical evaluation of data to determine if data are of the right type, quality, and quantity to support their intended use." DQA is more global in its purview than the previous verification and validation steps. DQA, in addition to reviewing the issues raised during verification and validation, may be the first opportunity to review other issues, such as field activities and their impact on data quality and usability. DQA should consider the combined impact of all project activities in making a data usability determination, which is documented in a DQA report.

1.5 The MARLAP Process

An overarching objective of the MARLAP Manual is to provide a framework and information for the selection, development, and evaluation of analytical protocols and the resulting laboratory data. The MARLAP process is a performance-based approach that develops APSs and uses these requirements as criteria for the analytical protocol selection, development and evaluation processes, and for the evaluation of the resulting laboratory data. This process, which spans the three phases of the data life cycle for a project—planning, implementation and assessment—is the basis for achieving MARLAP's basic goal of ensuring that radioanalytical data will meet a

project's data requirements. A brief overview of this process, which is referred to as the MARLAP process and is the focus of Part I of the manual, is provided below.

The MARLAP process starts with a directed planning process. Within a directed planning process, key analytical issues based on the project's particular analytical processes are discussed and resolved. The resolution of these key analytical issues produces the APSs, which include the MQOs. The APSs are documented in project plan documents (e.g., Quality Assurance Project Plans, Sampling and Analysis Plans). A SOW is then developed that contains the APSs. The laboratories receiving the SOW respond with proposed analytical protocols based on the requirements of the APSs and provide evidence that the proposed protocols meet the performance criteria in the APSs. The proposed analytical protocols are initially evaluated by the project manager or designee to determine if they will meet the requirements in the APSs. If the proposed analytical protocols are accepted, the project plan documents are updated by the inclusion or referencing of the actual analytical protocols to be used. During analyses, resulting sample and QC data will be evaluated primarily using MQOs from the respective APSs. Once the analyses are completed, an evaluation of the data will be conducted, including data verification, data validation, and data quality assessment with the respective MQOs serving as criteria for evaluation. The role of the APSs (particularly the MQOs, which make up an essential part of the APSs) in the selection, development, and evaluation of the analytical protocols and the laboratory data is to provide a critical link between the three phases of the data life cycle of a project. This linkage helps to ensure that radioanalytical laboratory data will meet a project's data requirements, and that the data are of known quality appropriate for their intended use. The MARLAP process is illustrated in Figure 1.3. Although the diagram represents the MARLAP process in a linear fashion, it is important to note that the process is an iterative one, and there can be many variations on this stylized diagram. Also, the phases shown at the right of Figure 1.3 only illustrate the relationship of the MARLAP process to the data life cycle.

1.6 Structure of the Manual

MARLAP is divided into two main parts. Part I provides guidance on implementing the MARLAP process as described in Section 1.5. This part of the manual focuses on the sequence of steps involved when using a performance-based approach for projects requiring radioanalytical laboratory work starting with a directed planning process and ending with DQA. Part I provides the overall guidance for using a performance-based approach for all three phases of a project. A more detailed overview of Part I is provided in Section 1.6.1. While the primary users for most of the Part I chapters are project managers and planners, other groups can benefit from the guidance in Part I.

Part II of the manual provides information on the laboratory analysis of radionuclides to support a performance-based approach. Part II provides guidance and information on the various activities performed at radioanalytical laboratories, such as sample preparation, sample

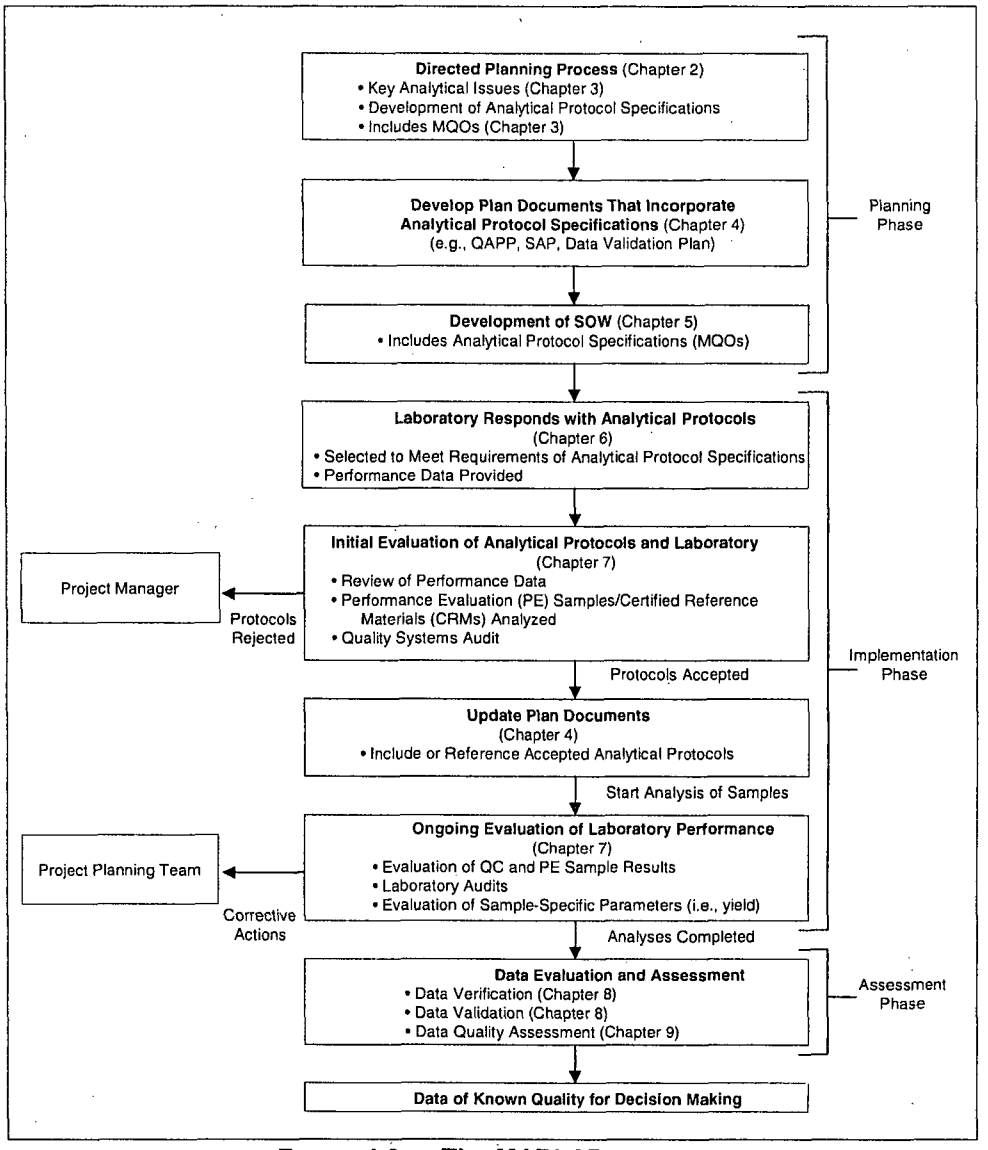

FIGURE 1.3 — The MARLAP process

dissolution, chemical separations, preparing sources for counting, nuclear counting, etc. The primary users for Part II are laboratory personnel. Using the overall framework provided in Part I, the material in Part II can be used to assist project planners, managers, and laboratory personnel in the selection, development, evaluation, and implementation of analytical protocols for a particular project or program. Figure 1.4 illustrates the interaction of the project manager and the laboratory using key MARLAP terms and processes. A more detailed overview of Part II is provided in Section 1.6.2. In addition to Part I and Part II, MARLAP has several appendices that support both Part I and Part II of the manual. An overview of the appendices is provided in Section 1.6.3 of this chapter.

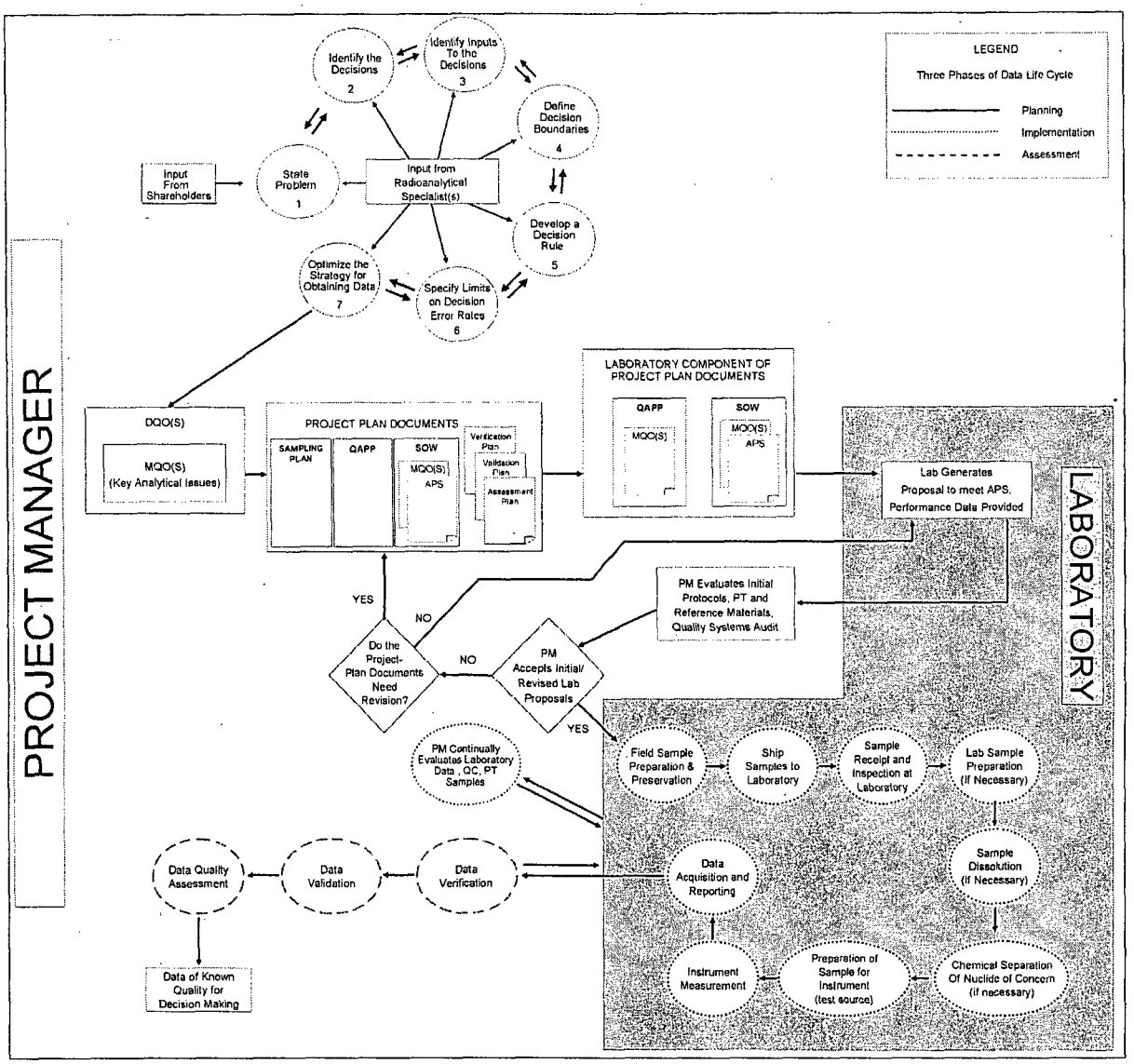

FIGURE 1.4 — Key MARLAP terms and processes

Because of the structure and size of the manual, most individuals will naturally focus on those chapters that provide guidance in areas directly related to their work. Therefore, to help ensure that key concepts are conveyed to the readers, there is some material is repeated, often in very similar or even the same language, throughout the manual.

1.6.1 Overview of Part I

Figure 1.3, the MARLAP Process on page 1-14, illustrates the sequence of steps that make up a performance-based approach for the planning, implementation, and assessment phases of radioanalytical projects. The remainder of Part I closely tracks this sequence:

- Chapter 2, *Project Planning Process,* provides an overview of the directed planning process and its outputs.

- Chapter 3, *Key Analytical Planning Issues and Developing Analytical Protocol Specifications*, describes key analytical planning issues that need to be addressed during a directed planning process and provides guidance on developing APSs, which are outputs of the planning process.

- Chapter 4, *Project Plan Documents*, provides guidance on the linkage between project planning and project plan documents, with an overview of different types of project plan documents (e.g., work plans, quality assurance project plans, sampling and analysis plans).

- Chapter 5, *Obtaining Laboratory Services*, provides guidance on developing a statement of work that incorporates the APSs.

- Chapter 6, *Selection and Application of an Analytical Method,* provides guidance on selecting or developing analytical protocols that will meet the MQOs and other requirements as outlined in the APSs. Unlike the rest of Part I, this chapter is intended primarily for laboratory personnel, because under a performance-based approach, a laboratory may use any protocol that meets the requirements of the APSs. (Other factors, such as cost, also will influence the selection of analytical protocols.)

- Chapter 7, *Evaluating Methods and Laboratories,* provides guidance on the initial and ongoing evaluation of analytical protocols and also provides guidance on the overall evaluation of radioanalytical laboratories.

- Chapter 8, *Radiochemical Data Verification and Validation,* provides an overview of the data evaluation process, provides general guidelines for data verification and validation, and provides "tools" for data validation.

- The last chapter of Part I, Chapter 9, *Data Quality Assessment,* discusses data quality assessment and provides guidance on linking data quality assessment to the planning process.

1.6.2 Overview of Part II

The chapters in Part II are intended to provide information on the laboratory analysis of radionuclides. The chapters provide information on many of the options available for analytical protocols, and discuss common advantages and disadvantages of each. The chapters highlight common analytical problems and ways to identify and correct them. The chapters also serve to educate the reader by providing a detailed explanation of the typical activities performed at a radioanalytical laboratory. Consistent with a performance-based approach, the chapters in Part II do not contain detailed step-by-step instructions on how to perform certain laboratory tasks, such as the digestion of a soil sample. The chapters do contain information and guidance intended to assist primarily laboratory personnel in deciding on the best approach for a particular laboratory task. For example, while the chapter on sample dissolution does not contain step-by-step instructions on how to dissolve a soil sample, it does provide information on acid digestion, fusion techniques, and microwave digestion, which is intended to help the reader select the most appropriate technique or approach for a particular project.

The primary audience for Part II is laboratory personnel and the chapters generally contain a significant amount of technical information. While the primary target audience is laboratory personnel, other groups, such as project planners and managers, can benefit from the guidance in Part II. Listed below are the chapters that make up Part II of the manual. It should be noted that Part II of the manual does not provide specific guidance for some laboratory activities that are common to all laboratories, such as laboratory quality assurance, and laboratory health and safety practices. This is primarily due to the fact that these activities are not unique to radioanalytical laboratories and considerable guidance in these areas already exists.

Chapter 10	Field and Sampling Issues That Affect Laboratory Measurements
Chapter 11	Sample Receipt, Inspection, and Tracking
Chapter 12	Laboratory Sample Preparation
Chapter 13	Sample Dissolution
Chapter 14	Separation Techniques
Chapter 15	Quantification of Radionuclides
Chapter 16	Data Acquisition, Reduction, and Reporting for Nuclear Counting Instrumentation
Chapter 17	Waste Management in a Radioanalytical Laboratory
Chapter 18	Laboratory Quality Control
Chapter 19	Measurement Uncertainty
Chapter 20	Detection and Quantification Capabilities

Chapters 10 through 16 provide information on the typical components of an analytical process in the order in which activities that make up an analytical process are normally performed. While not providing step-by-step procedures for activities such as sample preservation, sample digestion, nuclear counting, etc., the chapters do provide an overview of options available for the

various activities and importantly, provide information on the appropriateness of the assorted options under a variety of conditions.

Chapter 17, *Waste Management in a Radioanalytical Laboratory*, provides an overview of many of the regulations for waste disposal and provides guidance for managing wastes in a radioanalytical laboratory. Chapter 18, *Laboratory Quality Control,* provides guidance on monitoring key laboratory performance indicators as a means of determining if a laboratory's measurement processes are in control. The chapter also provides information on likely causes of excursions for selected laboratory performance indicators, such as chemical yield, instrument background, quality control samples, etc.

Chapters 19, *Measurement Uncertainty*, and 20, *Detection and Quantification Capabilities*, provide information on statistical principles and methods applicable to radioanalytical measurements, calibrations, data interpretation, and quality control. Topics covered in the chapter include detection and quantification, measurement uncertainty, and procedures for estimating uncertainty.

1.6.3 Overview of the Appendices

Seven appendices provide additional details on specific topics discussed in Part I and Part II chapters. Appendices A through E primarily support Part I chapters (project planning issues) and Appendices F and G primarily support the chapters in Part II (laboratory implementation issues).

- Appendix A, *Directed Planning Approaches,* provides an overview of a number of directed planning processes and discusses some common elements of the different approaches.

- Appendix B, *The Data Quality Objective Process,* provides an expanded discussion of the Data Quality Objectives Process including detailed guidance on setting up a "gray region" and establishing tolerable decision error rates.

- Appendix C, *Measurement Quality Objectives for Method Uncertainty and Detection and Quantification Capability,* provides the rationale and guidance for developing MQOs for select method performance characteristics.

- Appendix D, *Content of Project Plan Documents*, provides guidance on the appropriate content of plan documents.

- Appendix E, *Contracting Laboratory Services,* contains detailed guidance on contracting laboratory services.

- Appendix F, *Laboratory Subsampling,* provides information on improving and evaluating laboratory subsampling techniques.

- Appendix G, *Statistical Tables,* provides a compilation of statistical tables.

1.7 References

American Society for Testing and Materials (ASTM) D5792. *Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives*, 1995.

International Organization for Standardization (ISO). 1993. *International Vocabulary of Basic and General Terms in Metrology*. ISO, Geneva, Switzerland.

International Organization for Standardization (ISO). 1995. *Guide to the Expression of Uncertainty in Measurement.* ISO, Geneva, Switzerland.

MARSSIM. 2000. *Multi-Agency Radiation Survey and Site Investigation Manual, Revision 1.* NUREG-1575 Rev 1, EPA 402-R-97-016 Rev1, DOE/EH-0624 Rev1. August. Available at www.epa.gov/radiation/marssim/.

U.S. Environmental Protection Agency (EPA). 2000. *Guidance for the Data Quality Objective Process* (EPA QA/G-4). EPA/600/R-96/055, Washington, DC. Available at www.epa.gov/quality1/qa_docs.html.

18 LABORATORY QUALITY CONTROL

18.1 Introduction

This chapter addresses internal laboratory quality control (QC), the purpose of which is to monitor performance, identify problems, and initiate corrective action. If project requirements are more stringent than typical laboratory QC criteria, the project manager and the laboratory should confer to see whether the laboratory can accommodate the project QC requirements. Project QC requirements are addressed in Part I of MARLAP.

Laboratory data should be produced under a quality system[1] that incorporates planning, implementing, and internal assessment of the work performed by the laboratory, including QC. MARLAP fully endorses the need for a laboratory quality system and a quality manual that delineates the quality assurance (QA) policies and QC practices of the laboratory. A laboratory's quality system should ensure that laboratory processes and measurements are "in statistical control," which means that the distribution of measured results is stable.

This chapter's purpose is to provide guidance to laboratory staff on those activities and professional practices a radioanalytical laboratory should undertake to produce data of known quality. This chapter also shows how to use statistical techniques to monitor specific measures of the analytical process to indicate the level of control of the analytical process within the laboratory. These measures are called "performance indicators," and the statistical techniques involve the use of control charts. Monitoring performance indicators through control charts enables the identification of trends. The laboratory can then address analytical problems and help improve the analytical process. Section 18.3.2 and Attachment 18A at the end of this chapter provide examples of several types of charts. The use of statistical techniques is the preferred method for implementing quality control in the laboratory (Attachment 18B). The chapter also identifies specific performance indicators, the principles that govern their use, indications and underlying causes of excursions, statistical means of evaluating performance indicators, and examples of root-cause evaluations.

Contents

[1] A quality system is a structured and documented management framework that describes the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides for planning, implementing, and assessing the work performed by the organization and for carrying out required quality assurance and quality control (ANSI/ASQC E4, 1994). General requirements for testing laboratories can be found in ISO/IEC 17025.

This chapter addresses the control of the analytical process in the laboratory, as distinct from meeting the typical analytical needs of a specific project. Quality control provides quantitative estimates of analysis and measurement controls that can be used to determine compliance with project objectives.

18.1.1 Organization of Chapter

Chapter 18 has five major sections in addition to this introduction. Section 18.2 provides a general overview of QC and its application in the laboratory setting. Section 18.3 discusses the importance of evaluating performance indicators and provides statistical means for their evaluation. Sections 18.4 and 18.5 identify primary radiochemistry and instrumentation performance indicators, respectively, and discuss each in detail. Section 18.6 discusses other aspects of the analytical process that require scrutiny but are not formally considered performance indicators.

18.1.2 Format

The chapter is presented in a different format than the preceding chapters in order to highlight the performance indicators and to give examples. For each performance indicator, general guidance is provided in the format shown below.

Issue: Defines and summarizes the performance indicator

Discussion: Identifies those matters important to the performance indicator, including:

- What is the performance indicator and how does it work?
- Why is the performance indicator important, and what is its impact on the quality of the measurement?
- What is the relationship of the performance indicator and the combined standard uncertainty derived for the analytical method?
- What are the acceptable limits of the performance indicator?
- What are the key assumptions underlying the performance indicator?
- What limits and cautions are associated with the assumptions made?
- How sensitive is the quality of the measurement to the assumptions made?
- What is the appropriate frequency for assessing this performance indicator?

Excursions: "Excursions" are departures from the expected condition. This section addresses the likely types of excursions encountered during laboratory analysis and explains what each may indicate. This section also discusses the potential reasons for these excursions and the implications for the analytical results.

Examples: Where appropriate, this section provides typical examples of excursions, potential reasons for excursions, and additional information.

18.2 Quality Control

Quality control includes all technical activities that measure the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer. It also includes operational techniques and activities that are used to fulfill requirements for quality (ANSI/ASQC E4, 1994).

QC may not always detect blunders. Good laboratory practices, in addition to adherence to standard operating procedures (SOPs), are part of the overall QA/QC aspects needed to check the laboratory's performance. To monitor and control quality, laboratories use performance indicators, which are instrument- or protocol-related parameters that are routinely monitored to assess the laboratory's estimate of measurement uncertainty, precision, bias, etc. Initially, these parameters are used to maintain or demonstrate control over the analytical process. The performance indicators should be tracked by appropriate personnel. If the performance indicator control limits are exceeded, management should be informed and corrective action should be initiated.

Figure 18.1 lists some of the potential causes for radioanalytical control excursions. By no means is the list complete, and the reader should be aware of additional potential causes of excursions that are presented in the rest of this chapter and the other chapters. Many problems are complex and have multiple components that could complicate the search for causes of protocol or instrument related excursions. A metrologist or radiochemist should be consulted to identify and remedy any analytical problems.

18.3 Evaluation of Performance Indicators

18.3.1 Importance of Evaluating Performance Indicators

As stated previously, performance indicators are measures of the analytical process that the laboratory monitors as part of its routine QC program. Performance indicators demonstrate whether the analytical process is performing as planned, when it has exhibited a statistical anomaly that requires investigation, and when a system has failed. Accordingly, monitoring performance indicators using established statistical techniques provides the laboratory with an effective tool for self assessment that allows the identification of trends or conditions that, while still within the established bounds of acceptability, are drifting or trending out of control. These conditions can be addressed prospectively, allowing the laboratory to maintain analytical control.

Additionally, this process allows the development of a data base regarding a protocol's or system's behavior over time or under a specified set of conditions.

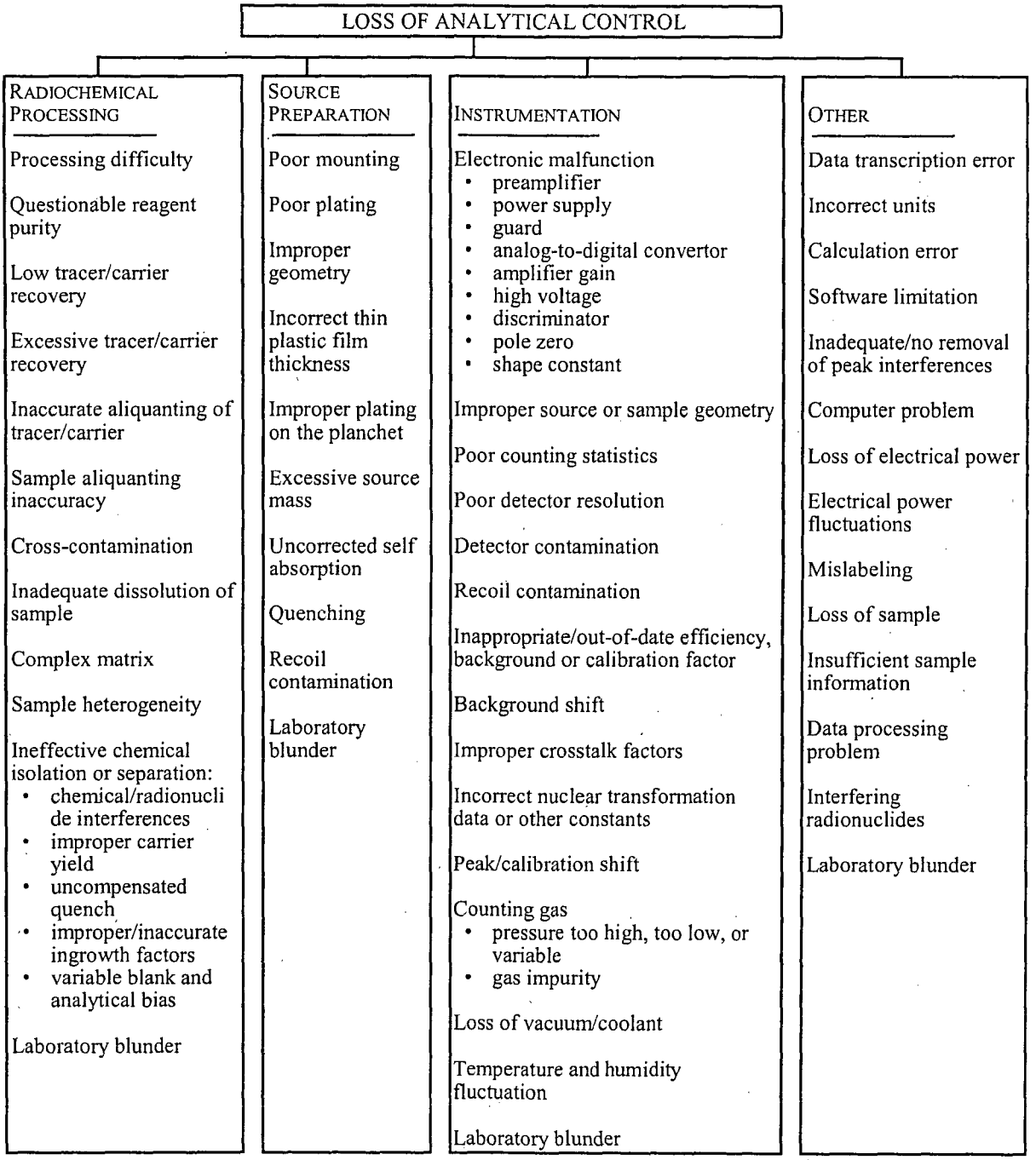

FIGURE 18.1 — Problems leading to loss of analytical control

18.3.2 Statistical Means of Evaluating Performance Indicators — Control Charts

The primary tool for statistical quality control is the control chart (see Attachment 18A). The theory that underlies a control chart is statistical hypothesis testing (see *NIST/SEMATECH e-Handbook of Statistical Methods*, http://www.itl.nist.gov/div898/handbook/, 2003). The implementation of a control chart makes the theory transparent to the average user and reduces the process of statistical inference to answering simple questions, such as, "Is the measured parameter greater than the upper control limit?" or "Is the measured parameter in the warning region?"

In theory, to test whether a parameter θ is above or below a certain value θ_0, a test statistic is defined and its distribution is determined under the assumption that $\theta = \theta_0$ (the null hypothesis). The value of the statistic is calculated and compared to critical values to test the assumption. In practice, a control chart is designed so that a non-statistician can perform these tests easily by comparing the measured value of the parameter to control limits and warning limits.

Most control charts do not implement hypothesis tests in a rigorous manner that allows decision error rates to be precisely determined. The charts are intended to be simple and practical tools for use even in situations where the assumptions needed for a rigorous test are not verifiable.

Every control chart has control limits, which define the acceptable range of the monitored variable. Many charts have both upper and lower limits. However, when changes in only one direction are of concern, only one limit is necessary. Most control charts have a central line, or reference line, which is an estimate of the expected value of the monitored variable. Many control charts also have warning limits, which lie between the central line and the control limits.

By definition, control limits are action limits. A single measured value that falls outside these limits normally requires that one stop the measurement process, investigate the problem, and if necessary take corrective action. The warning limits are optional but recommended, since they help one to identify and investigate possible problems before control limits are exceeded.

Types of Control Charts: Control charts based on grouped observations often are more powerful tools for detecting shifts of the monitored variable than charts based on individual observations. *Average charts*, or $\overline{X}$ *charts*, are used to monitor the arithmetic means of measured values obtained in "rational subgroups," which are subgroups of equal size chosen to ensure that the measurement variability within each subgroup is likely to represent only the inherent variability of the measurement process produced by non-assignable causes (see Attachment 18A). When an $\overline{X}$ chart is used, a *range chart*, or *R chart*, is generally used in tandem to monitor within-group variability. (The *range* of a set of values is the difference between the largest value and the smallest.)

A control chart for individual values (*X chart* or *I chart*) is used when it is impractical to obtain measured values in the groups needed for an $\overline{X}$ chart. In this case, a *moving range chart* (*MR chart*) is often used as well to monitor variability. The moving range chart is an *R* chart based on the absolute differences between consecutive measured values.

A control chart may or may not be based on a particular type of data distribution. Most control charts use limits derived from the normal distribution but are intended to be used for data with almost any distribution (ISO 8258). However, when data obtained from radiation counters are monitored, the Poisson distribution may often be assumed. The standard types of control charts for Poisson data in industrial applications are called "*c* charts" (for total counts) and "*u* charts" (for count rates). A third type of Poisson control chart, which is a variant of the *u* chart, is frequently used to monitor radiation counter efficiency. When the data distribution is Poisson, separate charts for monitoring the value of the parameter and its variability are generally unnecessary because the mean and variance of a Poisson distribution are numerically equal.

The following documents provide more guidance on the use of control charts:

- ASTM D6299. *Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance.*
- ASTM E882. *Standard Guide for Accountability and Quality Control in the Chemical Analysis Laboratory.*
- ANSI/ISO/ASQC A3534-2. *Statistics–Vocabulary and Symbols–Statistical Quality Control.*
- ISO 7870. *Control Charts – General Guide and Introduction.*
- ISO 7873. *Control Charts for Arithmetic Average with Warning Limits.*
- ISO 7966. *Acceptance Control Charts.*
- ISO 8258. *Shewhart Control Charts.*
- American Society for Testing and Materials (ASTM) MNL 7, *Manual on Presentation of Data and Control Chart Analysis* ASTM Manual Series, 7th Edition, 2002.

Figure 18.2 illustrates a typical control chart using counting data from analysis of a reference material (with limits corrected for decay) showing the statistical nature of the chart. The applicability of control chart techniques is based on the assumption that laboratory data approximate a normal distribution. The counting data plotted graphically represent the test results on the vertical axis and the scale order or time sequence in which the measurements were

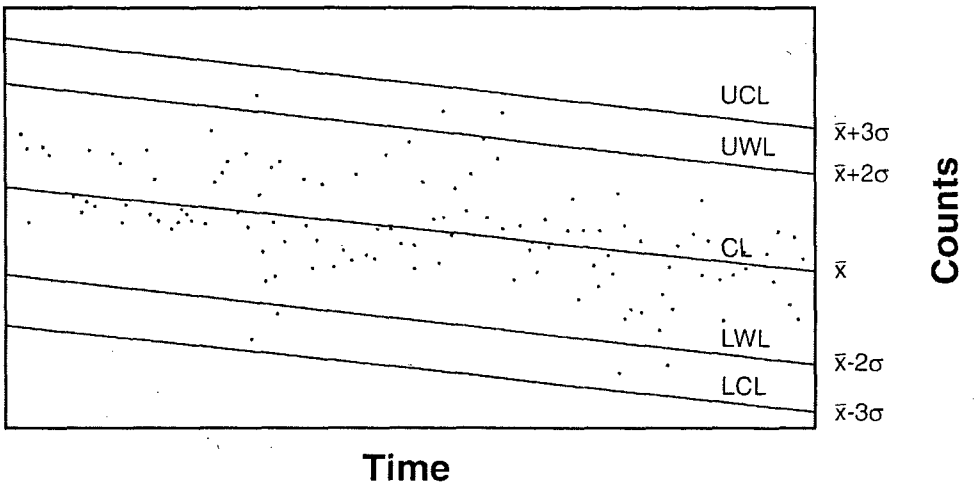

FIGURE 18.2 — Control chart for daily counting of a standard reference source, with limits corrected for decay

obtained on the horizontal axis. The mean of the measurements is represented by the central line (CL), and the limits of dispersion in terms of standard deviation are represented by the upper and lower warning and control limits (UWL, UCL, LWL, LCL). The warning limits are usually 2 standard deviations from the mean and the control limits are 3 standard deviations from the mean. See Attachment 18A for more discussion on establishing control charts.

18.3.3 Tolerance Limits

In some situations, the acceptance limits for a QC parameter may be based on professional judgment rather than statistics. MARLAP uses the term *tolerance limits* to refer to these judgment-based acceptance limits. (Note that this term has another meaning in statistics.) Tolerance limits are used much like the control limits on a control chart to determine whether investigation and corrective action are required. (They may also be called "go/no go limits.") Tolerance limits may be used when it is important to detect large changes in the variable. For example, tolerance limits could be used when variability within the limits has no significant impact on the measurement process.

An example of a variable that may sometimes appear to shift by small amounts is the resolution of a high-purity germanium detector. It also tends to be true that even statistically significant changes in the resolution are often so small that they have no practically significant effect on analytical results. So, it is reasonable to specify tolerance limits for the resolution (FWHM) rather than statistically based control limits.

Another example of a variable that is commonly monitored using tolerance limits is the chemical yield for an analytical process. Typically the yield is measured with relatively small uncertainty;

so, fluctuations of the yield over some range of values may have no substantial impact on the quality of the measurement. However, a yield that is significantly greater than 100 percent generally indicates a spurious error of some kind, and a yield that is very low may indicate a spurious error or other problem in the measurement process that deserves investigation (see Sections 18.6.4, "Interferences"; 18.6.5, "Negative Results"; and 18.6.7, "Calibration of Apparatus Used for Weight and Volume Measurements").

A graphical representation of the history of the monitored variable is useful even when control charts are not used. When the data are plotted on a graph with the tolerance limits drawn as lines (like the control limits on a control chart), the graph is sometimes called a *tolerance chart.*

18.3.4 Measurement Uncertainty

Issue: Every measured result is uncertain to some degree. If the measurement uncertainties are large relative to the tolerances needed for decision making, the data may not be useful for their intended purpose. A discussion of measurement uncertainty is contained in Chapter 19, and the terms used in this section are defined in that chapter and in the Glossary.

Discussion: In order to determine the significance of a sample result, all reported values should be accompanied by the laboratory's best estimate of the uncertainty associated with the result. The "combined standard uncertainty" (one-sigma uncertainty) is obtained by propagating the uncertainties of all the input quantities that contribute to the calculation of the derived value (Chapter 19).

The combined standard uncertainty is used to indicate the statistical confidence in interpreting the performance indicator's ability to assess analytical quality. The estimated statistical confidence level that is usually associated with 1 combined standard uncertainty is about 68 percent, the confidence level for 2 combined standard uncertainties is about 95 percent, and the confidence level for 3 combined standard uncertainties is about 99 percent. It is important that the combined standard uncertainty be a fair estimate because it will indicate when the analytical process could be approaching the limits of statistical control and corrective actions should be initiated. A performance indicator exceeding ±2 combined standard uncertainty limits from the indicator's historical mean value may indicate that corrective action should be considered, and a performance indicator exceeding ±3 combined standard uncertainty limits from the indicator's historical mean value may indicate that an investigation must be conducted and corrective action may be necessary. Because statistical confidence never reaches 100 percent, it probably would be prudent to confirm the measurement for the performance indicator when it exceeds ±2 combined standard uncertainty limits. If the performance indicator value for repeat measurements do not exceed ±2 combined standard uncertainty limits, one may conclude that the first measurement was a statistically allowable event. However, if the excursion is repeated, appropriate investigative actions should be considered.

Most of the significant sources of uncertainty in radiochemical data are known to a laboratory and can be estimated. These include uncertainties associated with sample and background counting, radiochemical yield determination, efficiency calibration, and blank assessment. Other less easily defined but significant sources of uncertainty include those associated with self-absorption and quench correction, sample density correction, sample geometry variation, gamma photopeak area determination, determination of sample volume or weight, and dead time correction.

The uncertainty of a measured value is controllable, within certain limits, by decreasing the uncertainty associated with some input parameters. For samples containing low levels of radioactivity, a large component of the combined standard uncertainty may be associated with the instrumental assessment (counting) of the sample aliquant, i.e., the standard uncertainty of the net count (gross sample count minus background count). Increasing the total net count accumulated, or decreasing the uncertainty of the instrument background, or both, will decrease the counting uncertainty. Changes that may be made to decrease the counting uncertainty include increasing the counting time for the sample or background, increasing the sample aliquant size (unless the sample geometry, quench, or self-absorption factors offset the gain in total radioactivity counted), using a more efficient geometry or detector, using an instrument with a lower background, and reanalyzing the sample to obtain a greater radiochemical yield. It also may be possible to concentrate the sample, which has the equivalent effect of increasing the sample aliquant size.

18.4 Radiochemistry Performance Indicators

Section 18.3 discussed how to evaluate radiochemistry performance indicators using statistically based control chart techniques. Any of the indicators below (blanks, replicates, laboratory control samples, matrix spikes, certified reference material, or tracer yield) can be evaluated using the control chart techniques. Analysts can use numerical performance indicators to identify loss of control. Control charts will assist laboratory personnel in identifying the quality trends and excursions of any performance indicator.

18.4.1 Method and Reagent Blank

Issue: A method blank is a sample of a matrix as similar as practical to the associated samples that is free from the analytes (radionuclides) of interest to the extent possible. The method blank is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedures. A reagent blank consists of the analytical reagent(s) in the procedure without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

Blank samples are used to determine whether any radionuclide contamination is introduced by the measurement process. They assist in the control of any contamination introduced by the

laboratory. Ideally, no target analytes should be present in the blank at detectable concentrations. If that is not possible (e.g., for naturally occurring radionuclides), those radionuclides should be extremely well-characterized and tracked. Control charts can be used to track these radionuclide levels in blanks. Using X charts, the laboratory can establish a program that evaluates the levels and trends of radionuclides in the different laboratory blanks. The techniques for establishing such a control chart program are described in Attachment 18A.

Discussion: The method blank is assumed to be representative of all samples in the batch with respect to the matrix and contamination assessment. When practical, it consists of the same or equivalent medium as the analytical samples, such as a deionized water blank for aqueous samples. Soil blanks are often prepared using "clean sand," commercially available fine-grained or beach sand whose inherent concentrations of target radionuclides are small and have been characterized sufficiently by the laboratory to allow its use as a blank. This approach may not be appropriate for very low-level analyses. Powdered, natural-matrix Standard Reference Materials (SRMs) are commercially available from the National Institute of Standards and Technology (NIST) and also may be suitable (Section 18.4.5). However, due to the natural variability of soils, each choice of method blank medium must be evaluated by the laboratory prior to use. The results of method blanks typically are not used to correct sample activities but only to monitor for contamination.

Reagent blanks are matrix-independent and assess any contamination only from the reagents and lab-ware. They may be used to correct sample activities for the contribution of naturally occurring radionuclides in the reagents, and used like method blanks, to check for unexpected contamination. The results of the reagent blank analyses should be reported separately by the analytical laboratory. How their values are used in determining the final sample results should be addressed during the final data assessment.

It is common practice for some laboratories to add the reagents into a volume of deionized water equal to the sample volume, while other laboratories simply add the required reagents to an empty container and process it as an analytical sample. In either case, it should be noted that the reagent blank is not monitoring the entire analytical process. The fundamental issue for each laboratory is to decide on the appropriate reagent blank necessary to obtain the needed information on the measurement system. Considerable variability exists among laboratories in the use and preparation of reagent blanks.

In general, the reagent blank's concentration of analyte is expected to be small compared to that of the sample. However, for some low-activity environmental samples this may not be the case, and the correction becomes increasingly important as the concentration of the analyte in the sample approaches background concentrations. In these cases, care should be taken to accurately quantify the levels of radionuclides in the reagent blanks.

It is important to minimize radionuclide concentrations in the blanks and bring these levels under control. This is usually achieved through careful selection of reagents, maintaining laboratory and counting areas free from contamination, and by segregating high and low activity samples. Thorough documentation of all blank values is essential to allow for the application of statistical tests to evaluate potentially anomalous values and delineate their extent.

Ideally, the analyte concentration in a method or reagent blank should be as close to zero as possible, and replicate measurement of the blanks should be consistent within counting statistics. Acceptance criteria for blank results should be established and applied to all data, and should include warning and control limits (Section 18.3.2, "Statistical Means of Evaluating Performance Indicators — Control Charts"). Blank values require scrutiny as part of the data evaluation and validation process for each analytical batch. Should restocking of reagents or other wholesale laboratory changes occur during a project, the method and reagent blanks prepared under the new conditions should be re-evaluated to ensure that they continue to be within established criteria.

An example of a numerical performance indicator for a method blank or a reagent blank used to monitor for unexpected contamination is

$$Z_{\text{Blank}} = \frac{x}{u_c(x)} \tag{18.1}$$

where x denotes the measured blank activity and $u_c(x)$ denotes its combined standard uncertainty. Warning limits for Z_{Blank} are ±2 and control limits are ±3. As mentioned earlier, if a reagent blank is used to blank-correct sample results, the blank results should be evaluated using control charts.

Typically, one method blank and/or reagent blank is analyzed with each batch or grouping of analytical samples regardless of batch size. Situations may occur where more frequent blanks are required to ensure that analytical conditions are stable, particularly when analyzing high and low concentration samples in the same analytical batch, or when instruments, reagents, or analytical method are suspect.

In general, corrective actions include procurement control of reagents, good laboratory cleaning practices, sample segregation according to anticipated concentrations, and instrument-related concerns, as discussed in this section. Good laboratory cleaning protocols should incorporate the evaluation of method and reagent blank performance to indicate if current practices are adequate. Instrument background data indicate a system's stability, and can be used to pinpoint the source of contamination, as can routine contamination (removable and fixed) surveys of laboratory and counting areas that are performed by the organization's health physics or radiation safety personnel.

Excursion: Blank changes can be grouped into three general categories: rapid changes, gradual increase or decrease, and highly variable changes. These are represented in Figure 18.3 and described below.

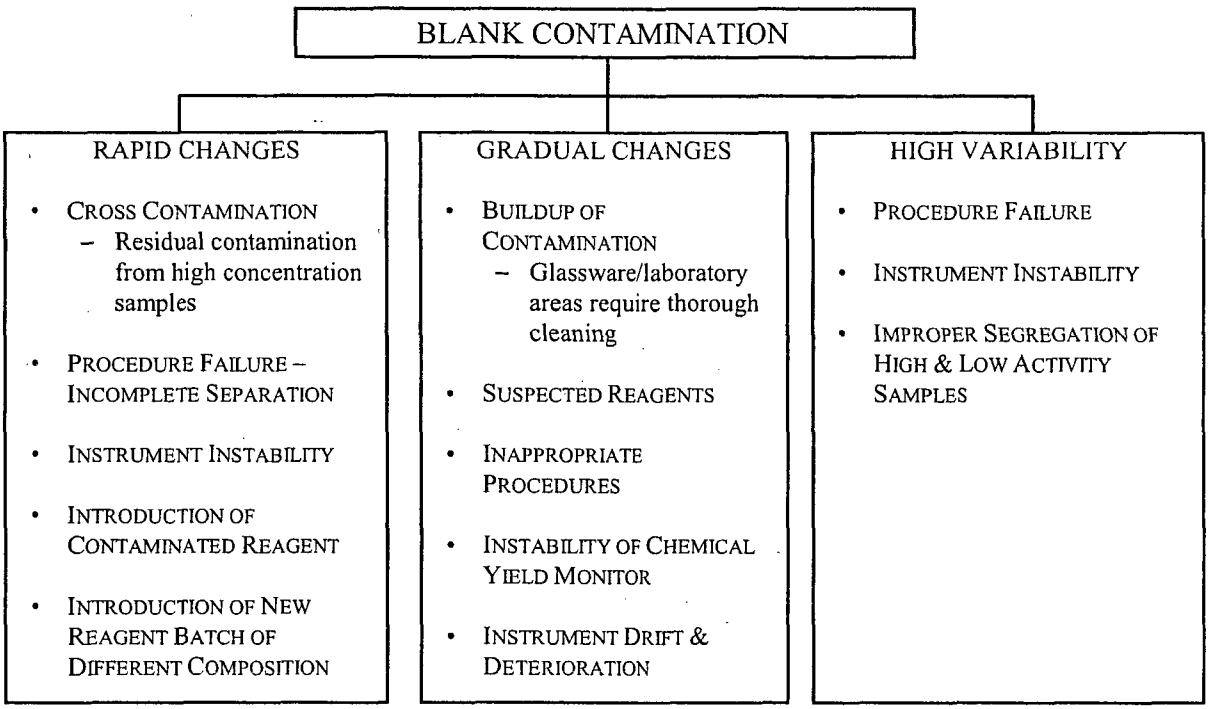

FIGURE 18.3 — Three general categories of blank changes

Rapid Changes: A sudden change in a blank value indicates the existence of a condition requiring immediate attention. Sudden changes often are caused by the introduction of a contaminant from high concentration samples, impure reagents, or contaminated sample preparation areas. Two potential sources of increased values in blanks are laboratory cleaning practices and contaminated reagents. A laboratory protocol should be established for cleaning and monitoring contamination from laboratory ware and equipment. Laboratory reagents, either as newly prepared solutions or from newly opened bottles, also can be a source of unexpected contamination. Significant increases in blank radioactivity should suggest these two as possible sources, and if confirmed, they should be corrected. Particular attention should be paid to the samples analyzed directly prior to the contaminated blank, since small amounts of residues from these samples can contaminate the instrument and have large effects on subsequent results when analyzing samples at or near environmental background. It may be necessary to take swipe or smear samples of questionable areas to identify the contaminant's source followed by a thorough cleaning or decontamination of all affected areas. Additionally, method or reagent blank values that are suddenly depressed should be investigated and may indicate other problems, including instrument malfunction like a loss of counting gas, incomplete chemical separation during the chemical preparation, or the failure to add necessary reagents. These other problems may be reflected in other areas, such as instrument performance checks or tracer yields.

Gradual Changes: Gradually increasing blank values indicate the need to inspect all sample preparation and counting areas for sources of residual contamination. Often housekeeping or routine contamination control details such as cleaning glassware or instrument counting chambers are sufficient to bring blank values under control. Alternatively, gradually decreasing blank values warrant scrutiny with respect to proper instrument settings and procedural related problems like a lack of tracer/sample exchange, failure of chemical separation reactions, or the addition of all necessary reagents. The importance of documenting method and reagent blank values in this regard cannot be overemphasized, since data evaluation and trending analyses are impossible without complete records.

High Variability: Because method blank values are expected to be near zero, the degree of variability they exhibit should reflect the statistical variation inherent in determinations near these levels. Large variations in blank values typically indicate problems related to instruments or the analytical process, as discussed in the two previous sections.

18.4.2 Laboratory Replicates

Issue: A laboratory replicate is two or more aliquants taken at the first subsampling event, normally after homogenization. In the event that there is no subsampling (when the method calls for using the entire sample) replicate analysis typically involves counting the prepared sample twice. The results of laboratory replicates are used to evaluate the method precision. Note that counting a sample twice only assesses the instrument portion of the measurement process.

Precision is a measure of agreement among replicate measurements of the same property under prescribed similar conditions. Precision is a fundamental aspect of the analytical process and should be evaluated routinely as part of the laboratory's quality system. Evaluation typically is performed using multiple analysis of the same sample (blanks, spikes, blinds, reference materials, performance evaluation samples, etc.), in whole or part, and evaluating the analyses relative to a statistically based criterion. The range of sample types requires that the sample matrix's effects on the precision be captured and evaluated by the laboratory's routine quality control practices. The reproducibility of analytical results should be evaluated by replicates to establish this uncertainty component.

Discussion: The purpose for measuring precision is to determine whether the laboratory can execute an analytical method consistently and thus obtain results of acceptable variability. Analytical samples cover a range of physical forms or matrices, from homogeneous samples like finished drinking water to complex soils or heterogeneous wastes, and each matrix has the potential to affect a protocol's precision.

In general, precision for aqueous samples tends to be less affected by sample heterogeneity than other media because if the sample's constituents are dissolved the sample is essentially homo-

geneous. This facilitates dividing the samples into equivalents fractions or aliquants. When appropriate, acidification of a sample to pH less than 2 should be done prior to dividing it for replicate analysis. Multi-phase and high-solid-content samples that are heterogeneous are more problematic.

The acceptance criterion for precision should be related to the combined standard uncertainties of the measured results. The uncertainty of a result may depend on many factors (e.g., dissolved solids in water or particle sizes of soil), but such factors should affect the acceptance criterion only through their effect on the standard uncertainty.

As an alternative to sample duplicates, a matrix spike duplicate is sometimes used as an indicator of the reproducibility of the analytical precision, as discussed in Section 18.4.3. A matrix spike duplicate is treated in the same manner as an unspiked replicate: both samples (original and duplicate) are processed identically to the other samples in the batch, and each aliquant is treated as an individual sample.

If the sample has multiple phases, the phases should be separated for individual analysis. For heterogenous materials, multiple analyses should be used, or the combined standard uncertainty of the results should be increased, to account for subsampling error (Appendix F). A typical frequency for replicate analyses is a minimum of one per analytical batch, regardless of batch size. "Batch" is defined as a given number of samples of similar matrix type with associated QC samples analyzed under the sample conditions at approximately the same time.

All analytical batches should be evaluated with respect to precision, whether by using replicates or matrix spike duplicates. This is done typically by the use of an acceptance criterion that derives a statistic that quantifies the difference between two values obtained by analyzing the same sample. Limits are then placed on the criterion, and data for any batch in excess of the criterion require investigation and corrective action as appropriate. An example of a numerical performance indicator for laboratory replicates is

$$Z_{\text{Rep}} = \frac{x_1 - x_2}{\sqrt{u_c^2(x_1) + u_c^2(x_2)}} \qquad (18.2)$$

where x_1 and x_2 denote the two measured activity concentrations and $u_c(x_1)$ and $u_c(x_2)$ denote their respective combined standard uncertainties. Warning limits for Z_{Rep} are ±2 and control limits are ±3.

Excursions: A regularly scheduled evaluation of precision with respect to the acceptance criterion should be an integral part of the laboratory quality system. Careful attention should be paid to the nature and anticipated analyte concentrations of all samples processed by the laboratory. Prospective identification of samples where precision is expected to be problematic often

can address difficulties in this area. The choice of appropriate analytical method and analyst training are also important. An analyst needs to be familiar with specific steps in the procedure that provide an indication of incomplete processing.

Precision exhibits a range of values and depends in part on sample matrix and activity, assuming correct execution of the analytical method. Small changes, positive and negative, are expected and should be captured in the acceptance criterion's range. It is also sensitive to sample heterogeneity or errors in processing, such as incomplete chemical separation or sample dissolution, and lack of tracer or carrier equilibration. When performance indicators for precision are outside acceptance criteria, the laboratory should determine the reasons why and implement corrective actions.

Certain samples will exhibit higher variability because of their matrix, or the proximity of their analyte concentration to ambient background, as discussed previously. Consideration should be given to cases where a matrix requires the development and implementation of a specific acceptance criterion. The main causes for lack of precision (Figure 18.4) can be grouped as follows:

- Laboratory subsampling — subsampling techniques produced two dissimilar aliquants from one sample, and the original and duplicate are not the same. An analyst should be careful to ensure that the sample is thoroughly homogenized before subsampling.

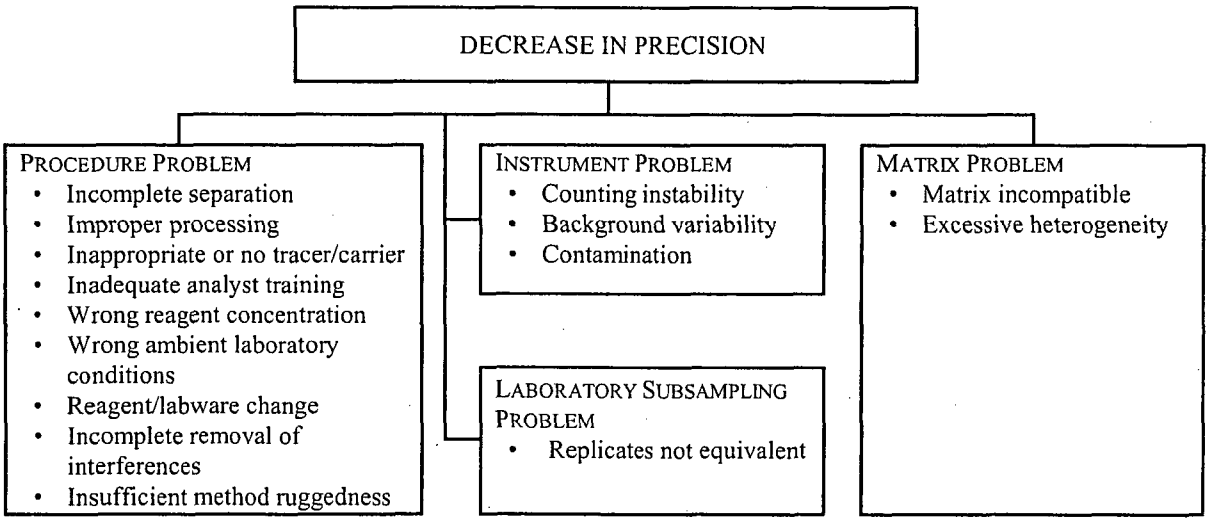

FIGURE 18.4 — Failed performance indicator: replicates

- Matrix – Sample constituents interfere with preparation chemistry, e.g., coprecipitation of interfering nontarget radionuclides from sample or excessive dissolved solids.

- Counting statistics – Sample activity is so low that small statistical variations in background

cause disproportionate responses.

- Contamination – Intermittent contamination from measurements system, glassware, etc., produces anomalous data for the original sample, but not the duplicate/replicate.

- Other – Failed chemical process, failed instrumentation, training, failed lab environment, failed procurement control.

18.4.3 Laboratory Control Samples, Matrix Spikes, and Matrix Spike Duplicates

Issue: A laboratory control sample (LCS) is a QC sample of known composition (reference material) or an artificial sample, created by fortifying a clean material similar in nature to the environmental sample. The LCS is prepared and analyzed in the same manner as the environmental sample. A matrix spike is typically an aliquant of a sample fortified (spiked) with known quantities of target radionuclides and subjected to the entire analytical procedure to establish if the method or procedure is appropriate for the analysis of a particular matrix. In some cases, specifically prepared samples of characterized materials that contain or are spiked with the target radionuclide and are consistent with the sample matrix may be used as matrix spikes. Matrix spikes should be used for those methods that do not include a radiotracer or internal carrier in the chemical separation process and where there is sufficient sample. A matrix spike duplicate (MSD) is a second-replicate matrix spike that is used to evaluate the method precision. Matrix spike duplicates are used in a similar fashion as laboratory sample replicates, but in cases where there are insufficient quantities of target radionuclides in the laboratory sample replicates to provide statistically meaningful results.

An important performance indicator is the ability to ensure that the analytical methods employed obtain data that are representative of the true activity in a sample, i.e., produce data that are accurate. The routine analysis of spiked samples provide data for an evaluation of the laboratory's reported measurement uncertainty and allow for the determination of bias, if one exists. Evaluation is typically performed using prepared samples consisting of media equivalent to a routine analytical sample with a known, measurable amount of the analyte of interest. Upon completion of the analysis, the results are compared to the known or accepted value, and the agreement is evaluated using a predetermined criterion. The range of sample types assayed in a laboratory may require the preparation of spikes using several sample media. Use of matrix spiked samples will reflect the analytical method's ability to make accurate quantitative determinations in the presence of the matrix.

Discussion: As stated previously, analytical samples cover a range of physical forms or matrices, and each matrix can change a method's expected accuracy. Tracking sets of LCS and matrix spike results can give laboratory personnel an indication of the magnitude of an observed method bias. Care must be taken when analyzing site specific matrix spike results because these matrices

may be very complex and subject to large variability. In general, the variability of matrix spikes in aqueous samples tends to be less affected than other media like soils or heterogeneous mixtures. However, multi-phase or high-solid-content fluids and brackish or saline waters may be more problematic.

The analyst should carefully consider the spiking levels for laboratory control samples and matrix spikes. Spikes and LCSs may be prepared near the lower limits of detection to test the method's performance on clean samples or samples containing small quantities of the target analytes. Conversely, matrix spikes and LCSs may be spiked at high levels for samples having high concentrations of target analytes. The laboratory should try to spike at or near the action level or level of interest for the project.

Examples of numerical performance indicators for laboratory control samples and matrix spikes are

$$Z_{\text{LCS}} = \frac{x - d}{\sqrt{u_c^2(x) + u_c^2(d)}} \tag{18.3}$$

$$Z_{\text{MS}} = \frac{x - x_0 - d}{\sqrt{u_c^2(x) + u_c^2(x_0) + u_c^2(d)}} \tag{18.4}$$

where x is the measured value of the spiked sample, d is the spike concentration added, x_0 is the measured concentration of the unspiked sample, and $u_c^2(x)$, $u_c^2(d)$, and $u_c^2(x_0)$ are the squares of the respective standard uncertainties. The warning limits for either of these indicators are ±2 and the control limits are ±3.

Excursions: Excursions in the LCSs and MSs can be used to identify various out of control situations. The advantage to the LCS is that the sample matrix is always the same so matrix effects should not be a factor in evaluating excursions. A rapid and one-time excursion in the LCS usually indicates that a mistake was made in the procedure. A rapid change with continued occurrences suggest that something occurred that is out of the ordinary, such as a new analyst performing the procedure or a new standard solution or new reagents being used. If an LCS shows elevated concentrations, analysts should check for contamination sources or poorly prepared spiking solutions. Slow changes showing a trend usually indicate degradation or contamination of equipment or reagents and may be indicative of bias and should be investigated.

Excursions of MSs can be difficult to interpret if the matrix changes from batch to batch. However, an excursion may indicate that the method is not appropriate for a particular matrix. If the MS shows lower than expected concentrations, the analyst should check for poor techniques or expired or poorly prepared reagents and spiking solutions. When the chemical yield of a

process is determined through a stable isotopic carrier, lower-than-expected analyte concentrations may result from inherent quantities of the stable isotope in the sample matrix.

Elevated or depressed results for site-specific MSs need to be interpreted in conjunction with the results from LCSs. If both the LCS and site-specific MS results are elevated or depressed then the cause is usually internal to the laboratory. If only the site-specific MS is depressed or elevated, the cause usually is due to the matrix.

18.4.4 Certified Reference Materials

Issue: Certified reference materials (CRMs) are well-characterized, stable, homogeneous materials with physical or chemical properties that are known within specified uncertainty limits. Laboratories that analyze CRMs can compare their performance to the certified concentration and uncertainty levels. CRMs are used for the calibration of an apparatus or the assessment of a measurement method.

Discussion: Metrology organizations issue CRMs in various matrices with critically evaluated concentration values for the radionuclide constituents. A CRM issued by NIST or under license from NIST is called a "standard reference material" (SRM). The usefulness of a reference material depends on the characterization of the radionuclide source, activity levels, and their estimated uncertainties.

CRMs can be used as internal laboratory QC samples to evaluate the ability of analytical methods to handle the matrix. CRMs need not be known to the analyst but can be introduced into the analytical stream as a blind. Comparison of analytical results of CRMs to their certified values provides linkage to the NIST radioactivity primary standards and a measure of method accuracy.

The planning that goes into the preparation of a CRM involves the selection of analytical techniques that have adequate sensitivity and precision for specific analyses. It has become increasingly important to have available well-characterized CRMs of a natural "matrix" type, which may be used in laboratory tests of measurements of environmental radioactivity. Such materials may be used in the evaluation of competing analytical methods, and also in the cross-comparison of interlaboratory data—both at the national level and the international level.

The Ionizing Radiation Division of NIST has constructed several SRMs for radiation measurements. These are included in the 4350 series and can be ordered through NIST. One widely used SRM is the natural matrix ocean sediment (4357). The radionuclides in the NIST natural matrix SRMs are not spiked into the matrix but are incorporated through natural processes to present the analyst with the combination of species that may be faced on a routine basis. SRM 4357 has two sediment sources: the Chesapeake Bay (benign) and the Irish Sea ("hot").

The NIST natural matrix SRM project has certified actinides, fission and activation radionuclides in soils, freshwater lake and river sediments, human tissues, and ocean sediment, and is working on additional unique matrices: ashed bone, ocean shellfish, and Rocky Flats Soil-II.

A numerical performance indicator for the analysis of a CRM is essentially the same as that for a laboratory control sample. An example is

$$Z_{CRM} = \frac{x - d}{\sqrt{u_c^2(x) + u_c^2(d)}} \tag{18.5}$$

where x is the measured value, d is the certified value, and $u_c^2(x)$ and $u_c^2(d)$ are the squares of the respective combined standard uncertainties. Warning limits for Z_{CRM} are ±2 and control limits are ±3.

Excursions: Excursions in the CRM results can be used to identify various out-of-control situations. The advantage of the CRM is that the sample matrix is always the same, and the levels of analytes are known to a high degree, so uncertainties in matrix effects and radionuclide content should not be a factor in evaluating excursions. A rapid and one-time excursion in the SRM usually indicates that a mistake was made in the procedure. A rapid change with continued occurrences suggest that something occurred that is out of the ordinary, such as a new analyst performing the procedure or the use of a new batch of calibration solutions or reagents. Slow changes showing a trend usually indicate degradation or contamination of equipment or reagents.

If a CRM result shows elevated concentrations, analysts should check for contamination sources or poor instrument or tracer calibration. If the results show decreased concentrations, the analyst should check for poor techniques or expired or poorly prepared reagents and solutions.

CRM results may indicate a bias in the measurement process. Tracking the performance of several consecutive CRM measurements will show if the method or the laboratory consistently obtains high or low results. If the results are consistently higher or lower than the certified values, they should be evaluated for a statistical difference, e.g., *t*-tested. When the test indicates a statistical difference, a bias is indicated and the laboratory should investigate the cause of the bias and correct or characterize it.

Example: The NIST ocean sediment SRM 4357 offers a good example of a material for evaluating a laboratory performance using a specific analytical method. The blended sediment sample has been analyzed by a number of laboratories, and 10 radionuclides have certified activity values (Lin et al., 2001). The six "natural" radionuclides concentrations tended to have normal distributions (Table 18.1a), while the four "man-made" radionuclides tended to have Weibull distributions (Table 18.1b). There are also 11 other radionuclides where the activity concentrations are not certified at this time but may be at some future time (Table 18.1c).

TABLE 18.1a — Certified Massic activities for natural radionuclides with a normal distribution of measurement results

Radionuclide	Mean ± $2s_m$ * (mBq/g)	Tolerance Limit (2.5 to 97.5%) (mBq/g)	Number of Assays
^{40}K	225 ± 5	190 – 259	31
^{226}Ra	12.7 ± 0.4	10.3 – 15.0	21
^{228}Ra	13.3 ± 0.8	9.2 – 17.4	20
^{228}Th	12.1 ± 0.3	9.7 – 14.6	40
^{230}Th	12.0 ± 0.5	9.6 – 14.4	18
^{232}Th	13.0 ± 0.3	11.6 – 14.3	18

Table 18.1b — Certified Massic activities for anthropogenic radionuclides with a Weibull distribution of measurement results

Radionuclide	Mean ± $2s_m$ * (mBq/g)	Tolerance Limit (2.5 to 97.5%) (mBq/g)	Number of Assays
^{90}Sr	4.4 ± 0.3	2.1 – 8.4	49
^{137}Cs	12.7 ± 0.2	10.8 – 15.9	76
^{238}Pu	2.29 ± 0.05	1.96 – 2.98	65
$^{239}Pu + ^{240}Pu$	10.4 ± 0.2	9.3 – 13.2	84

Table 18.1c — Uncertified Massic activities. Radionuclides for which there are insufficient data or for which discrepant data sets were obtained. Uncertainties are not provided because no meaningful estimates could be made.

Radionuclide	Mean (mBq/g)	Range of Reported Results (mBq/g)	Number of Assays
^{129}I	0.009	0.006 – 0.012	6
^{155}Eu	1.4	1.2 – 1.5	2
^{210}Po	14	12 – 15	5
^{210}Pb	24	14 – 35	19
^{212}Pb	14	13 – 14	5
^{214}Bi	15	9 – 20	5
^{234}U	12	9 – 15	68
^{235}U	0.6	0.1 – 1.4	63
^{237}Np	0.007	0.004 – 0.009	9
^{238}U	12	7 – 16	76
^{241}Am	10	7 – 18	97

SRM 4357. Data for these radionuclides are provided for information only. The Massic activities are not certified at this time, but they may be certified in the future if additional data become available.

* S_m = standard uncertainty of the mean.

18.4.5 Chemical/Tracer Yield

Issue: Some methods require that radionuclides should be separated chemically from their sample matrix and purified before measurement. During chemical processing, some of the analyte radionuclide will be lost due to sample spillage, evaporation, incomplete chemical reactions (i.e., precipitation or extraction), etc., as discussed in Chapter 12. While these losses may correlate with a group of samples of similar chemical composition or from the same sampling area, they can be sample specific. For quantitative analysis, it is necessary to correct observed instrument responses for these losses for each analytical sample. Corrections are made using compounds that are stable (carriers) or radioactive (tracers). An inappropriate method for determining chemical yield may result in an analytical bias.

Discussion: Most alpha- and beta-emitting radionuclides require chemical separation prior to measurement, in part because of the short effective range of the radiation.

CARRIERS. Since it is impossible to determine exactly how much of the analyte is lost during processing, and because the physical mass of the radionuclide is too small to measure gravimetrically, a compound is added to the sample at the start of the chemical processing, and is carried through the analytical process and assayed. The added compound typically is stable and exhibits the same chemical properties as the analyte and therefore "carries" the analyte radionuclide—for example, stable barium that carries radium isotopes, or stable yttrium that carries ^{90}Y. These added compounds are called "carriers" and are added in sufficient quantity to allow gravimetric assay upon completion of the analysis. The ratio of the carrier recovered to the amount added is the chemical recovery, or yield. Because the carrier and analyte exhibit similar chemical behavior, the chemical yield of both should be equal, i.e., if 85 percent of the stable barium is recovered, then it follows that the observed instrument response represents 85 percent of the radium present in the sample.

TRACERS. For radionuclides above atomic number 83, stable isotopes do not exist, and a different approach often is taken to determine the analyte's yield. For these radionuclides, an isotope other that those being measured is added to the sample in the same manner as described above, e.g., ^{232}U used as a tracer for isotopic uranium (^{234}U, ^{235}U, and ^{238}U), ^{236}Pu, or ^{242}Pu used as a tracer for isotopic plutonium (^{238}Pu, ^{239}Pu, and ^{240}Pu).

This approach to chemical yield determination is based on the following assumptions regarding the carrier/tracer:

- It exhibits similar chemical behavior as the analyte under the protocol's conditions.
- The energy emission of the tracer and progeny should not interfere with the resolution of the analytes of interest.

- It is chemically and physically equilibrated with the sample before losses of either occur.
- Indigenous concentrations of carrier or tracer are insignificant, or are well known and can be quantified and corrected for during subsequent data analysis.
- The chemical form of carrier or tracer precipitates are consistent with what was used during the material's preparation and standardization.

Care should be taken during the analytical procedure to ensure that these assumptions are valid. Different conditions, such as a lack of equilibrium between the tracer and sample analyte, can result in inaccurate data. If there is indigenous tracer or carrier in the sample, this quantity should be known so that the appropriate correction can be made for its contribution to the chemical yield. In some cases, this will prevent the procedure's use, as described below. As stated previously, the quantity of tracer or carrier added to the sample should overwhelm its indigenous concentration, which cannot be determined for samples with unknown tracer or carrier content. A separate analysis for trace elements or interfering radionuclides could provide information to estimate the uncertainty contributed by the sample's indigenous tracer or carrier.

It should be noted that some analytical methods exclude direct assessment of the procedure's chemical yield for each sample analysis. In such cases, chemical yield typically recovery is addressed by analyzing a group of prepared standards by the same protocol and the results are analyzed statistically to derive a chemical yield factor. The recovery factor is applied to routine samples based on the assumption that the standards used for its derivation are representative of routine samples. This approach precludes the empirical assessment of a sample specific chemical yield, and would probably require scrutiny and periodic verification.

Acceptance limits for chemical/tracer yields should be specified in the laboratory's quality manual. While it is customary to establish lower limits for chemical yield, upper limits may also be necessary since excessive yields indicate a loss of analytical control. All limits developed by the laboratory should be either statistically based or based on historical data, and should include warning and control limits. The inherent differences among sample matrices generally require the use of matrix specific criteria, i.e., finished drinking water limits may differ from limits for high solid content waters, sandy soils or heterogeneous media. Irrespective of medium, where practical, the chemical yield and its uncertainty should be determined, recorded and tracked for each radiochemical measurement.

Excursions: There are several possible reasons for the yield to be outside of the acceptance limits. These are summarized in Figure 18.5 and discussed below.

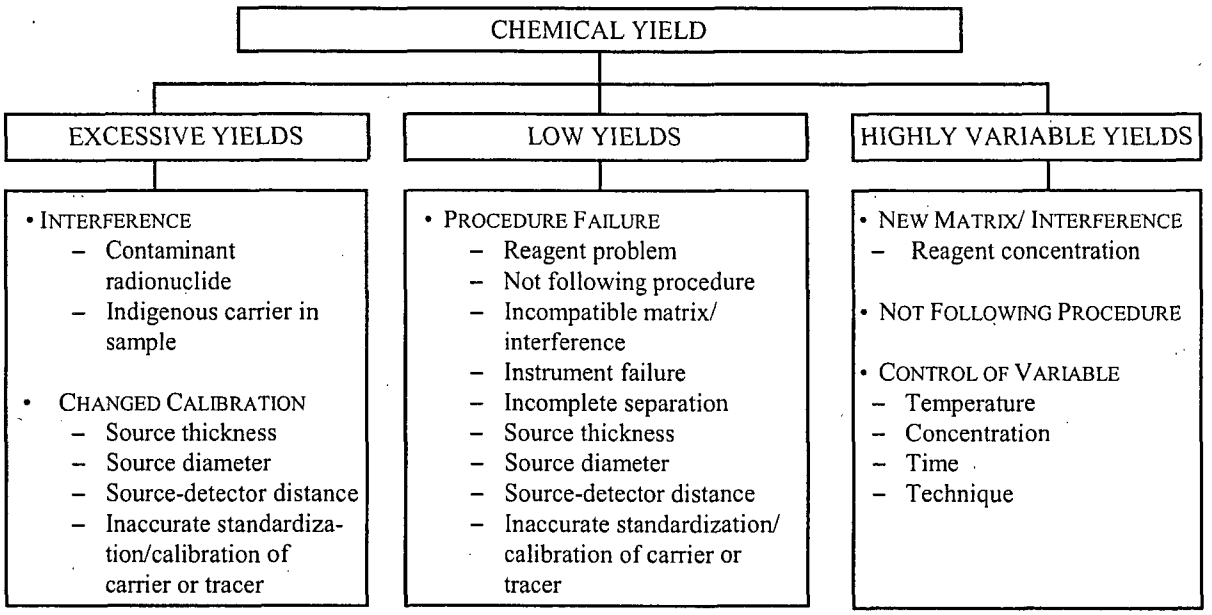

FIGURE 18.5 — Failed performance indicator: chemical yield

EXCESSIVE YIELDS: A chemical yield significantly greater than 100 percent indicates a problem. Typical causes of excessive chemical yields are provided below:

- Interference. The sample may contain an interfering radionuclide that cannot be distinguished from the tracer and therefore biases the tracer response; the sample may contain an indigenous concentration of the tracer or carrier used; or large amounts of another stable element are present.

- Counting. Changes in instrument calibration factor or other factors that affect counting, e.g., source thickness, diameter, source-detector distance or change in chemical form of final sample precipitate.

- Instrument failure.

LOW YIELDS: A very low yield usually indicates a procedural failure caused by incomplete or unsuccessful chemical separation, matrix interference, missing reagents, or the exclusion of a key element in the sample processing. A significantly lower yield will increase the overall measurement uncertainty and degrade the procedure's effective detection capability unless the counting time is appropriately extended, which may be impractical or even ineffective in many cases. Furthermore, measurement of the recovered carrier or tracer becomes increasingly more adversely affected by background, stable element, water absorption, and other corrections as the yield decreases. Fixed lower limits for yields often are established and

should be specific to analytical procedures and sample matrices. Setting an upper limit is recommended for the acceptable relative uncertainty in a yield measurement.

HIGHLY VARIABLE YIELDS: High variability in procedural temperature, concentration, time, reagent concentration, or laboratory technique can have dramatic effects on yield. Highly variable yields indicate a lack of procedural control and should be investigated and corrected. A simple step such as heating samples on a hotplate can lead to variability in yield because the hotplate surface is thermally uneven. Samples can be dried and reconstituted several times during the course of the preparation protocol, and samples may require different amounts of heat or water, which introduces additional variability. When highly variable chemical yields are observed, a careful examination of the analytical procedure's application is recommended to determine critical variables and the controls needed to re-establish adequate management over yields.

18.5 Instrumentation Performance Indicators

Radiometric and non-radiometric instruments are used currently to quantify radionuclides in a variety of environmental matrices, and quality control measures are necessary to ensure proper instrument performance. This section presents radiometric instrument performance measures that indicate a measurement system is in control. For detailed information on instrument concepts and specific techniques, see Chapter 15 as well as ASTM standard practices (e.g., D3648, for the Measurement of Radioactivity). The specific quality control procedures to be followed depend on the measurement equipment. Sufficient checks are needed to demonstrate that the measurement equipment is properly calibrated, the appropriate background has been recorded, and that all system components are functioning properly. QC measures for instrumentation should include at a minimum: (1) instrument background measurements, (2) instrument calibration with reference standards, and (3) periodic instrument performance checks subsequent to the calibration. Acceptable control limits should be specified in appropriate laboratory documents.

18.5.1 Instrument Background Measurements

Issue: In general, radionuclide detection covers more than 17 orders of magnitude of sample activity, from irradiated material that produces high radiation fields to environmental samples. All radiation detection instruments have a background response even in the absence of a sample or radionuclide source. To determine the instrument's response to the radioactivity contributed by the sample alone (net), the instrument background response is subtracted from the sample-plus-background response (gross). Background corrections become more critical when the instrument net response is small relative to the background. Careful control of contamination and routine monitoring of instrument background are therefore integral parts of a control program. Inappropriate background correction results in analytical error and will increase the uncertainty of data interpretation.

Discussion: Every radionuclide detector produces a signal response in the absence of a sample or radionuclide source. These signals are produced by electronic dark current, cosmic radiation, impurities in the instrument construction materials, crosstalk between the detector's alpha and beta channels, sources in the general vicinity of the detector, and residual contamination from previous counting episodes. The majority of these contributors (i.e., dark current, cosmic radiation, construction material impurities) to instrument background produce a fairly constant count rate, given sufficient measurement time. For other sources, instrument backgrounds vary as a function of time (i.e., from decay or ingrowth of residual contamination or as radon levels fluctuate throughout the day and season). For low-level measurements, it is imperative that the background be maintained as low as feasible. Active or passive detector shielding, removing or adequately shielding radioactive sources in the vicinity of the detector, and good laboratory practices to prevent residual contamination are necessary to maintain low instrument background.

The instrument's background should be determined in the absence of a radionuclide source. The instrument background should be well characterized. The instrument background is an important factor in determining the ability to achieve a specific minimum detectable concentration (MDC). Control limits for the background should be specified in appropriate laboratory documents. The background population considered in the statistical calculations should cover a sufficient period of time to detect gradual shifts in the measurement system's background contamination or detector instability. Additionally, backgrounds should be determined in such a way that they mimic actual sample measurement conditions as closely as possible, i.e., using appropriate sample containers, geometries, and counting times.

Background measurements should be made on a regular basis and monitored using control charts. For instruments with well established background performance records and a low probability of detector contamination, this frequency may be modified by the laboratory. For mass spectrometry and kinetic phosphorimetry analysis, background measurements should be performed on a real time basis. See ASTM E181, ANSI N42.12, and NELAC (2002) *Quality Systems Appendix D* for more information on the suggested frequency of background measurement.

Excursions: Variations in instrument backgrounds may indicate instrument malfunction. Variations may take the form of rapid increase or decrease in background, slow increase or decrease in backgrounds, and highly variable or erratic backgrounds. These variations can result in the measurement system's reduced precision and decreased detection capability. Rapid or significant increases in background measurements may be due to instrument or blank contamination, insufficient shielding with relocation of nearby radionuclide sources, or large scale equipment malfunction (e.g., a broken window on a gas proportional system).

Instrument background data should be evaluated for trends, which is facilitated by regular inspection of control charts. A slowly changing background could alert laboratory personnel to a potentially serious instrument failure. A sufficient number of data points (Chapter 15) taken over

time should be included in any trend analysis. Slowly changing instrument backgrounds could be caused by low counting-gas flow rates, small incremental instrument contamination, or electronic drift or noise.

When the instrument background is more variable than expected, the reliability of measurements becomes questionable, resulting in loss of confidence and increased uncertainty. This indicates a loss of control over the measurement environment, or limitations of the data handling software. The root cause of the variability should be identified and corrected to re-establish statistical control over the instrument background. Table 18.2 presents reasons for changing backgrounds.

TABLE 18.2 — Instrument background evaluation

Instrument Background Failed Performance Indicator		
Rapid Change in Background	**Slow Change in Background**	**Excessively Variable Background**
Electronic failure	Instrument contamination	Sources being moved
Detector failure	Electronic drift	Radon fluctuation
Loss of coolant/vacuum	Low counting gas flow rate	Insufficient shielding
Instrument contamination		Insufficient counting statistics
Counting gas changes		Interfering radionuclides
Temperature/humidity fluctuation		Poor peak deconvolution
Laboratory contamination		Intermittent electrical grounding problems
External sources		Failing electronics
Insufficient shielding		
Personnel with nuclear medicine dose		

18.5.2 Efficiency Calibrations

Issue: This section discusses selected aspects of instrument calibration that are pertinent to laboratory quality control. A more in-depth, technical discussion is provided in Chapter 16. The number of events (counts) recorded by a detector is converted to activity (actual radionuclide transformations) by empirically determining this relationship with NIST-traceable radionuclide sources when available. This relationship is expressed in the system's efficiency calibration. A separate efficiency is determined for each detector-source combination and is typically energy or radionuclide specific.

Detector efficiency is critical for converting the detector's response to activity. As discussed above, routine performance checks can evaluate several aspects simultaneously (sample geometry, matrix, etc.) and provide a means to demonstrate that the system's operational parameters are within acceptable limits. These are typically included in the assessment of the analytical method's bias and are specified in terms of percent recovery based on the source's known disintegration rate. Performance checks for measurement efficiency are usually determined statistically from repeated measurements with a specific check source. Detection of a shift in measurement efficiency should be investigated.

The frequency of performance checks for efficiency calibrations is instrument specific. The frequency of these checks is often based on a standardized time scale or a percentage of the total number of analyses performed using that method.

Performance checks for instrument efficiency typically are performed on a day-of-use basis. The level of activity in the check source should be sufficient to allow the accumulation of enough counts in a short time so that daily performance checks do not impose an unnecessary burden on the laboratory. However, the source strength for spectrometry systems should be such that instrument dead time is not significant and gain shifts do not occur (ANSI 42.23). For detectors that are used infrequently, it may be necessary to perform a check before and after each set of measurements.

Control charts provide a useful tool for documenting and evaluating performance checks for efficiency calibrations, and should be established and maintained for the intrinsic efficiency of each detector. There are several methods available for evaluating performance using control charts (see Attachment 18A).

Discussion: Most radiation detectors do not record all of the nuclear transformations that occur in samples undergoing measurement, i.e., they are not one hundred percent efficient. This occurs for several reasons, and the prominent reasons are discussed briefly below.

- Intrinsic or absolute efficiency[2] – In the absence of all other factors, a detector will only record a fraction of the emissions to which it is exposed due to its composition and other material-related aspects. Intrinsic efficiency is a measure of the probability that a count will be recorded when a particle or photon of ionizing radiation is incident on a detector (ANSI N1.1).

- Geometry – The spatial arrangement of source, shielding, and detection equipment, including the solid angle subtended by the detector and sample configuration, largely determines what fraction of the emissions from the source actually reach the detector (ANSI N15.37). Geometry includes the source's distance from the detector and its spatial distribution within the counting container relative to the detector and shielding components.

- Absorption – Radiation emitted by the source can be absorbed by the source itself (self-absorption), as well as other materials placed between the source and the detector, i.e., source container, detector housing, and shielding (NCRP 58).

[2] Efficiency measures the fraction of emitted photons or particles that are actually detected. It is affected by the shape, size, and composition of the detector as well as by the sample-to-detector geometry. There are two ways that efficiency can be expressed: "Absolute efficiency" is the fraction of all the photons or particles emitted by the source that are actually detected, and "intrinsic efficiency" is the ratio of photons or particles detected to the number that actually fall on the detector.

- Backscatter – Radiation emitted by the source can hit the source container or detector shielding and scatter into the detector.

The detector response is a composite of these factors.

Each radiation detector should be calibrated to determine the relationship between the observed count rate of the detector and the emission rate of the source being assayed. This relationship is called the efficiency calibration—typically expressed in counts per second/emissions per second, or cps/dps—and is an integral part of the measurement protocol. For alpha spectrometry systems, the efficiency of detection is energy-independent. Efficiencies for gamma spectrometry are energy dependent, and an efficiency calibration typically covers a range for a specific counting geometry, e.g., 50 to 1,800 keV.

Once this relationship is established, it should be checked at regular intervals using what is called a performance or calibration check. The performance check does not seek to reestablish the detector's efficiency but simply demonstrates that the relationship is within acceptance limits. When designed properly, an efficiency performance check evaluates the intrinsic efficiency, geometry and absorption in a single measurement. Accordingly, it takes the form of a single value that incorporates all effects for a target radionuclide and a specific detector-sample configuration. Detectors that are energy dependent and measure radionuclides with multiple energies, such as photon or alpha spectrometers, should have performance checks at several energies throughout the measurement range. For these detectors, the performance check can simultaneously address the system's efficiency, energy calibration and resolution using a single source. An internal pulser can be used to check the electronics.

Because the performance check's purpose is to demonstrate that the system's efficiency remains constant, the source's absolute disintegration rate need not be known, provided its purity can be established, its half-life is known, and its activity is sufficient to provide adequate precision. Accordingly, it is not necessary to use a NIST-traceable check source for this purpose. Check sources that are non-NIST-traceable can meet the precision objectives of the performance check and they are less expensive.

Excursions: Changes in the efficiency of a detector can only be corrected by determining the root cause of the problem and repeating the efficiency calibration. Gradual changes in geometry usually indicate a problem with the technique of sample mounting or preparation. A visual inspection of the prepared source is often helpful in eliminating sample geometry as a cause of the problem. For example, a precipitated sample counted on a gas proportional counter has an expected appearance, i.e., a circle of precipitate centered on the planchet and often covered with thin plastic film. If the prepared source does not have the correct appearance, there could be a problem with the geometry, self-absorption, and backscatter. This can sometimes be corrected by

preparing the source a second time, inspecting it and presenting it for counting a second time. Re-training personnel responsible for the error may also be indicated. Because sources that have been improperly prepared for counting can result in contamination of or physical damage to the detector, it is strongly recommended that every source be visually inspected prior to counting. Significant changes in geometry caused by modifications to the source preparation method can only be corrected by recalibrating the detector. Examples of modifications to source preparation methods are (1) using a new filter so that the geometry of the test source is different than the geometry used for calibration, and (2) replacing the containers used for gamma spectrometry with containers that have a different wall thickness or are made from different materials.

Changes in intrinsic efficiency generally result from a physical change to the detector and often result in rapid changes in efficiency. In many cases, changes that affect the intrinsic efficiency of a detector render it inoperable. These are specific to a detector type and are listed below:

- HPGe, Ge(Li), and surface barrier detectors – Real or apparent changes in intrinsic efficiency may be caused by vacuum leaks or failure of field effect transistor.

- Thin window detectors (gas proportional counters, low-energy photon) – Changes in measurement efficiency are typically associated with damage to the detector window.

- Gas proportional systems – Problems may be related to the quality or flow of counting gas.

- Anti-coincidence systems with guard detectors – Electrical problems with the anti-coincidence circuits may produce apparent changes in efficiency.

- Scintillation detectors – Gradual changes in efficiency are associated with the scintillator or the photomultiplier tube. For example, NaI(Tl) crystals may gradually turn yellow over time resulting in a lower intrinsic efficiency, and liquid scintillation counters may have residue gradually build up on the surface of the photomultiplier tube affecting the detection of photons by the tube.

18.5.3 Spectrometry Systems

18.5.3.1 Energy Calibrations

Issue: This section discusses selected aspects of instrument calibration that are pertinent to laboratory quality control. A more in depth, technical discussion of instrument calibration is provided in Chapter 15 (*Quantification of Radionuclides*). All radiation measurements are energy dependent to a certain extent. However, spectrometric techniques such as gamma and alpha spectrometry identify radionuclides based on the energy of the detected radiations. For these techniques a correct energy calibration is critical to accurately identify radionuclides. Problems

with energy calibration may result in misidentification of peaks.

Discussion: Spectrometry systems should be calibrated so that each channel number is correlated with a specific energy. To identify radionuclides correctly, this energy calibration needs to be established initially and verified at regular intervals. The energy calibration is established by determining the channel number of the centroid of several peaks of known energy over the applicable energy range. Typically, a minimum of three peaks is used, and commercially available sources contain nine or ten photopeaks. The relationship between energy and channel number can be determined by a least squares fit. To account for non-linearity, a second or third order fit may be used. However, these require more points to define the curve. For example, a first order calibration requires at least two points, while a second order calibration requires a minimum of three points. The end points of the curve define a range of applicability over which the calibration is valid, and peaks identified outside the curve's range should be used carefully. The uncertainty associated with the curve should be available at any point along the calibration curve.

Quality control checks for energy calibration may be combined with checks for efficiency calibration and resolution. Radiations emitted over the range of energy of interest are measured, and two or more peaks are used to demonstrate that the energy calibration falls within acceptable limits. Check sources may consist of a single radionuclide or a mixture of radionuclides (e.g., mixed gamma). Because only the location of the peak is of concern, there is no requirement that the check source be calibrated or certified, except for ensuring that it does contain the radionuclide(s) of interest at a specified level of purity.

The energy calibration is determined when the system is initially set up by adjusting the gain of the amplifier, analog-to-digital conversion (ADC) gain, and zero. Criteria that indicate when readjustment is required because of gradual and abrupt changes in the energy versus channel calibration should be established as an integral part of the system's operating procedure. These changes usually are monitored by the measurement system's software, and the user specifies the allowable difference between that the system's response and the radionuclide's known energy. The tolerable difference often relates to the instrument's resolution. For example, a high resolution instrument such as an intrinsic germanium detector typically will have acceptable limits on the order of a few keV, while a low resolution instrument such as a NaI(Tl) detector typically will have acceptable limits on the order of several tens of keV.

Spectra also can be analyzed by identifying each peak manually. With manual identification, the acceptable limits for the energy calibration are determined for each spectrum based on the professional judgment of the person analyzing the spectrum.

The frequency of QC checks for energy calibrations can be related to the expected resolution of the instrument, the electronic stability of the equipment, or the frequency needs of QC

measurements for efficiency calibration or resolution. These are specified typically in the laboratory's quality manual or other typical project-related documentation. Examples for three detector types are provided below and in Tables 18.5 through 18.8.

- HPGe and Ge(Li) Photon Detectors. Energy calibrations are typically verified using a check source on a day of use basis. Every source spectrum should include verification of the energy calibration as part of the data review process, when possible. Under extreme conditions (e.g., *in situ* measurements in bad weather), it may be necessary to perform checks at the beginning and end of each measurement period or day the instrument is used.

- Surface Barrier Alpha Spectrometry Detectors. The energy calibration is often performed using an alpha source when the instrument is setup initially and when a detector has been serviced or replaced. Electronic pulsers can be used for daily checks on energy calibration. Most alpha spectra include a chemical yield tracer with a peak of known energy that can be used to verify the energy calibration during data review. Alpha spectrometers have a lower resolution than germanium detectors, and newer spectrometers are sufficiently stable to allow weekly or monthly performance checks. The frequency of performance checks should be based on the number and frequency of measurements and historical information on the stability of the instrument.

- Low-Resolution NaI(Tl) Detectors. These typically are less stable than HPGe detectors and may require more frequent quality control checks, depending on the conditions under which they are used.

For all detectors where energy calibrations are performed daily, plotting the channel numbers of peak centroids can be useful for identifying trends and determining the need for adjusting the system. Changes in peak location may result in mis-identification of radionuclides. When this is observed, all spectra obtained since the last acceptable energy calibration check should be reviewed. If there is sufficient information within the spectrum to determine the acceptability of the energy calibration, no further action may be required for that spectrum. If the spectrum contains too few peaks of known energy, reanalysis should be initiated.

Gradual changes in peak location are not unexpected and the rate of these gradual changes can be used to establish the appropriate frequency of energy calibration checks. The acceptable limits on peak location established during the initial system setup may be used to indicate when the energy calibration needs to be readjusted.

Excursions: Changes in the energy calibration can be the result of many factors including power surges, power spikes, changes in the quality of the electrical supply, variations in ambient conditions (e.g., temperature, humidity), physical shock to the detector or associated electronics, and electronic malfunction.

Rapid changes in energy calibration are usually caused by power surges, power spikes, or physical shocks to the system. Corrective actions typically involve recalibrating the system and repeating the analysis. If changes result due to loss of cryostat vacuum, the instrument may need to be returned to the manufacturer to be refurbished or replaced.

Gradual changes in the energy calibration are usually the result of a variable or poorly conditioned power source, changes in the ambient conditions, or electronic malfunction. Corrective actions generally begin with identifying the root cause of the problem. Gradual changes that begin following relocation of the instrument are more likely to be caused by the power source or the ambient conditions. Installing a line conditioner, surge protector, and uninterrupted power supply is recommended to address problems related to the system's electrical power source. Problems with low humidity can be corrected through the use of a humidifier in dry climates or cold weather; conversely, high or variable humidity may require the use of a dehumidifier. Problems associated with fluctuations in temperature may require significant changes to the heating and cooling system for the room or building containing the instrument in order to stabilize the temperature. Gradual changes that occur following physical shocks to the system or following a rapid change in peak location with an unidentified cause are more likely to be the result of problems with the electronic equipment. In most cases the amplifier is the source of these problems, but the analog-to-digital converter, pre-amplifier, power supply voltages, and multi-channel (or single-channel) analyzer may also cause this type of problem. However, they could also be the result of crystal or detector failure. Systematic switching out of components and discussions with the instrument manufacturer will often help to identify which component may be the source of the trouble. It may be especially difficult to identify the source of problems with new instruments in a new facility.

18.5.3.2 Peak Resolution and Tailing

Issue: The shape of the full energy peak is important for identifying radionuclides and quantifying their activity with spectrometry systems. Poor peak resolution and peak tailing may result in larger measurement uncertainty. If consistent problems with peak resolution are persistent , then an analytical bias most likely exists. Many factors will affect peak resolution and these are discussed below.

Discussion: Detectors with good resolution permit the identification of peaks which are close in energy. When a monoenergetic source of radiation is measured with a semiconductor, scintillation, or proportional spectrometer, the observed pulse heights have a Gaussian distribution around the most probable value (Friedlander et al., 1981). The energy resolution is usually expressed in terms of the full width at half maximum (FWHM) or the full width at tenth maximum (FWTM).

In a semiconductor detector, fluctuations in output pulse height result from the sharing of energy

between ionization processes and lattice excitation (Friedlander et al., 1981). The number of charge pairs created by radiation of a given energy will fluctuate statistically. This fluctuation occurs because the energy causes lattice vibrations in the semiconductor as well as the formation of charge pairs. This sharing of energy causes a variation in the number of charge pairs created and gives rise to the width of a measured peak. The magnitude of the statistical fluctuation is proportional to the energy of the radiation. There is also a variation in the number of charge pairs collected by a detector.

In a scintillation detector, the statistical fluctuations in output pulse heights arise from several sources. The conversion of energy of ionizing radiation into photons in the scintillator, the electronic emission at the photocathode, and the electron multiplication at each dynode are all subject to statistical variations. Note that the distance of the source to the detector also impacts the resolution.

In a proportional counter, the spread in pulse heights for monoenergetic rays absorbed in the counter volume arises from statistical fluctuations in the number of ion pairs formed and the gas amplification factor (Friedlander et al., 1981). If the gas gain is made sufficiently large, the fluctuations in the number of ion pairs determine the resolution.

The FWHM typically is used as a measure of resolution, while the FWTM is used as a measure of tailing for the full energy peak. For Gaussian peaks with standard deviation σ, the FWHM is equal to 2.35σ. The resolution of a detector is the ratio of the FWHM (in keV) to the energy (in keV) at the most probable peak height. The sources of fluctuations that contribute to the standard deviation are dependent on the type of detector (see Chapter 15, *Quantification of Radionuclides*, for a more detailed discussion of detector resolution).

Resolution affects the ability to identify individual peaks in two ways (Gilmore and Hemingway,1995). First, it determines how close together two peaks may occur in energy and still be resolved into the two components. Second, for gamma spectrometry, when a peak of small magnitude sits on the Compton continuum of other peaks, its ability to be detected can depend on its signal-to-noise ratio. With good resolution, the available counts are distributed in fewer channels, thus those counts will be more easily identified as a peak by the spectrometry analysis software. If resolution degrades significantly the efficiency may be in error. This is especially true when the spectrum analysis involves the region of interest (ROI) concept. When the calibration is performed, the full energy peak may fit within the defined ROI limits, whereas the resolution degraded peak may have counts which fall outside them. Thus, the detector efficiency will be effectively decreased and inconsistent with the previously determined efficiency.

Tailing is another observable feature of the peak shape. Tailing is an increased number of counts in the channels on either side of the full energy peak. Tailing affects the FWTM more than the FWHM, so the ratio of FWTM to FWHM can be used as a measure of tailing. For a Gaussian distribution the ratio of FWTM to FWHM is 1.823. For most germanium detectors this ratio

should not exceed 2.0. Tailing may be caused by imperfect or incomplete charge collection in some regions of the detector, escape of secondary electrons from the active region of the detector, electronic noise in the amplification and processing circuitry, loss of vacuum and escape of bremsstrahlung from the active region of the detector. Tailing may also result from the source's self-absorption for alpha emitting radionuclides.

The resolution (FWHM) is routinely calculated for gamma and alpha spectrometry peaks by the spectrum analysis software and can be monitored by observing the FWHM calculated for the check sources routinely counted. Resolution monitoring and charting is normally an integral part of a measurement quality system. Acceptance parameters may be established for resolution and incorporated in the analysis software. For alpha spectrometry, where radionuclide tracers are used for chemical yield determination, the FWHM can be monitored for each analysis, if desired. Some projects may specify FWHM limits for internal tracer peaks on each sample run.

The shape of the peak is important for quantifying the activity, and resolution is important for identifying peaks in a spectrum. The shape of the peak is also important for monitoring the performance of a detector. Germanium detectors have very good resolution on the order of 1 percent. The FWHM at specific energies is provided by the manufacturer. The FWHM should be established at several energies throughout the range being measured because the FWHM is directly proportional to the energy. These energies are usually the same as those used for checking the energy calibration and the efficiency calibration. Tolerance or ontrol limits for FWHM and the ratio of FWTM to FWHM may be developed based on statistics using multiple measurements collected over time.

The resolution of an alpha spectrum is dominated typically by self-absorption in the source. This is indicated by low energy tailing and elevated FWTM and FWHM. Most surface barrier detectors are capable of resolutions on the order of 30-40 keV for monoenergetic nuclides and 80-100 keV for unresolved multiplets. Acceptance of sample resolution is usually monitored by visual inspection of individual spectra. For well-prepared samples, the FWHM of the alpha peaks may be expected to be from 30 to 80 keV.

The resolution of scintillation detectors is not as good as the resolution of semiconductor detectors, but peak shape and tailing are just as important for analyzing samples. The FWHM should be established at several energies throughout the range being measured. These energies are usually the same as those used for checking the energy calibration and the efficiency calibration. Control limits for FWHM and the ratio of FWTM to FWHM may be developed based on statistics using multiple measurements collected over time.

Performance checks for resolution and tailing should be performed for all instruments used as spectrometers. These measurements are usually combined with the performance checks for energy calibration and efficiency calibration. Quality control activities should include visual inspection of all spectra to evaluate peak shape and tailing.

Tolerance limits or control charts for FWHM and the ratio of FWTM to FWHM can be developed and used to monitor the performance of any detector used as a spectrometer. Because the concern is when the resolution degrades (i.e., the FWHM increases) or tailing becomes a problem (i.e., the ratio of FWTM to FWHM increases), control limits are necessary. Limits can be developed based on historical performance for a specific type of detector. Control charts offer a convenient method for monitoring the results of the performance checks. As mentioned previously, the concern is associated with an increase in the FWHM or the ratio of FWTM to FWHM. This means that only an upper control limit or tolerance limit is required for the chart.

Excursions: Changes to the FWHM are associated with malfunctioning or misadjusted electronics, excessive electronic noise or interference, or detector or source problems. Electronics problems include changes in the high voltage applied to the detector, noise (including cable noise and high voltage breakdown), and electronic drift. Electronics problems may be caused by changes in the high voltage, improper adjustment of the pole zero or baseline restorer, or drift of the amplifier gain or zero during acquisition. Source problems are usually only associated with alpha spectra and result in excessive self-absorption resulting in low-energy tailing. This can result in counts being identified with an incorrect peak. Problems that are not electronic or source related imply that the detector is malfunctioning.

Changes to the ratio of FWTM to FWHM indicate problems associated with tailing. Tailing can occur on the high- or low-energy side of the peak. High-energy tailing indicates electronics problems that may be caused by excessive activity in the sample, incorrect adjustment of the pole zero or pile-up rejector, or drift of the amplifier gain or zero while acquiring the spectrum. Low-energy tailing indicates an electronic or a source problem—a possible corrective action is to check to see if the vacuum is set properly for alpha detectors. Table 18.3 lists common problems, the implied root cause of the problem, and possible corrective actions.

TABLE 18.3 — Root-cause analysis of performance check results for spectrometry systems

Observed Problem	Implied Root Cause	Possible Corrective Actions
Efficiency changed	Unknown Electronics degradation Geometry changed Poor source Software application	Ensure the correct check source was used Check to ensure the efficiency was evaluated using the correct geometry Ensure high voltage is set properly Pulser check of electronics
Peak centroid moved	Gain changed	Check amplifier gain Check conversion gain Check stability of amplifier for gain shifts or drifting
	Offset shifted	Check zero offset Check digital offset Check stability of amplifier for gain shifts or drifting
FWHM changed	Electronics problem	Ensure high voltage is set properly
	Source problem	Increased source-to-detector distance (for alpha spectrometry)

Observed Problem	Implied Root Cause	Possible Corrective Actions
FWTM changed	Electronics problem	Ensure high voltage is set properly
	Source problem	Repeat test-source/sample preparation and recount Reanalyze sample Check with weightless (plated) source Increased source-to-detector distance (for alpha spectrometry)
No peak or broad peaks	Electronics problem	Ensure that high voltage is correct
Low-energy tailing	Electronics problem	Ensure that high voltage is correct Check pole zero adjustment Check baseline restorer Check stability of amplifier for gain shifts or drifting Check for loss of vacuum
	Source problem	Repeat test-source/sample preparation and recount Reanalyze the sample
High-energy tailing	Electronics problem	Check pole zero adjustment Check pile-up rejector Check stability of amplifier for gain shifts or drifting
	Source problem (too much activity)	Reduce volume of sample analyzed Increase distance between the source and detector
Spectra shifted uniformly	Offset shifted	Check zero offset Check digital offset Check amplifier for zero drift
Spectra stretched or compressed	Gain changed	Check amplifier gain Check conversion gain Check amplifier for gain shifts

18.5.4 Gas Proportional Systems

18.5.4.1 Voltage Plateaus

Issue: The accuracy of the results produced by a gas proportional system can be affected if the system is not operated with its detector high voltage properly adjusted, such that it is on a stable portion of the operating plateau.

Discussion: The operating portion of a detector plateau is determined by counting an appropriate source at increasing increments (e.g., 50 volts) of detector high voltage. For detectors which will be used to conduct analyses for both alpha- and beta-emitting radionuclides, this should be done with both an alpha and beta source. The sources used should be similar in both geometry and energy to that of the test sources to be counted in the detector.

A plot of the source count rate (ordinate) versus high voltage (abscissa) rises from the baseline to a relatively flat plateau region, and then rises rapidly into the discharge region for both the alpha

and beta determinations. From the plateau, the operating voltage is selected so that small voltage changes will only result in minor fluctuations to detector efficiency. Operation of the counter at the upper end of the plateau is not recommended and can result in the generation of spurious discharge counts. Modern high-voltage supplies, operating properly, experience little actual voltage fluctuation. The detector response should be checked after repairs and after a change of gas. The detector plateau should again be determined and plotted (voltage vs. count rate) after repairs, particularly to the detector unit.

The historical tracking of the establishment and maintenance of this operating parameter is recommended; it aids in determining the probable cause of quality control failure and the identification of long-term instrument deterioration. Items to be recorded include date/time, instrument detector designation, source number, check source response at the operating point, and pertinent instrument parameters, such as lower level discriminator setting, alpha-discriminator setting, length of the plateau, operating high voltage setting, etc.

Excursions: Voltage changes of short- or long-term duration will affect reliability of a proportional counter. If the detector voltage is lowered sufficiently, there is a danger of operating below the plateau knee which, in effect, reduces the efficiency and would bias the results of any sample count low. Should the voltage applied to the proportional detector be driven up to a point where the slope of the plateau is sufficiently great enough to increase the efficiency of the detector, sample counts may be biased high. A transient voltage increase of great enough magnitude could introduce spurious counts.

Shifts in the operating voltage along the plateau or length of the plateau could also result from long-term detector deterioration or electronic drift or failure.

18.5.4.2 Self-Absorption, Backscatter, and Crosstalk

Issue: The accuracy of alpha and beta activity determinations in samples with discernable solids in a gas proportional system depends in large part on the determination and maintenance of self-absorption and crosstalk curves.

Discussion: Samples counted for alpha and beta activity in a gas proportional system are typically prepared as inorganic salts, e.g., nitrates, carbonates, oxides, sulfates, or oxalates, and contain on the order of tens to hundreds of milligrams of solids when counted, which result in absorption and scattering of the particles in the sample material and mounting planchet (Chapter 16). Thus, for gas proportional systems, the detection efficiency for a given test source depends on the self-absorption occurring within each sample volume/mass. To establish the correction factor, a calibration curve is generated using a series of calibration sources consisting of an increasing amount of solids and known amounts of radionuclide. The relative efficiency for each calibration source is plotted against the amount of solids, and these data are used to determine a

test source's efficiency as a function of test-source mass. The diameter and the composition of the test-source planchet, not just the test-source mass, should be identical with what was used for routine samples. This allows calculation of the corrected amount of activity regardless of the test-source mass (mass/efficiency curves).

The counting of alpha and beta particles simultaneously in a proportional counter requires that an electronic discriminator be adjusted, such that pulses of heights below that represented by the discriminator are registered as betas, and those of greater heights are counted as alphas. Crosstalk occurs when alpha particles are counted in the beta channel or betas are registered as alphas. For example, the alpha-to-beta crosstalk for ^{241}Am, which also has a 59.5 keV gamma-ray emission (35.9 percent), would be greater than the alpha-to-beta crosstalk factor for a pure alpha emitter (such as ^{210}Po). However, this relationship is energy dependent, and care should be taken to identify samples that differ significantly from the sources used to establish the crosstalk ratio. For example, ^{90}Sr + ^{90}Y ($E_{\beta max}$ 2.28 MeV) is typically used as a beta source for instrument calibration. However, samples containing natural uranium in equilibrium with its progeny produce beta emissions that are considerably more energetic from the 3.28 MeV $E_{\beta max}$ betas of ^{214}Bi. The crosstalk ratio established with ^{90}Sr will be inadequate for such samples.

As the amount of solids in the test source increases, the beta crosstalk can increase due to the degradation of the alpha particle energy by interaction with test-source material. Similarly, the beta into alpha crosstalk decreases. Thus, crosstalk should be evaluated as a function of sample weight to correct the observed relative alpha and beta counts. This is normally determined in conjunction with the self-absorption curve. To check these parameters, calibration sources should be prepared at the low and high ends of the calibration curve, and the limit of their acceptability should be better than 1 percent (one sigma). These checks should be performed annually, at a minimum, and following detector replacement or significant repair. The historical tracking of the establishment and maintenance of these operating parameters is recommended. This aids in determining the probable cause of quality control failure and the identification of long-term instrument deterioration. In addition, items to be recorded include date/time, instrument detector designation, source number, operating point, and pertinent instrument parameters, such as lower level discriminator setting, alpha discriminator setting, etc.

Excursions: Any change in the detector-source geometry or adsorption characteristics between the source and detector, can affect the self-absorption and crosstalk correction factors. For example, the replacement of a detector window with one whose density thickness is different from the original window can necessitate the reestablishment of these parameters. Electronic drift of the alpha discriminator can also affect the crosstalk ratios.

18.5.5 Liquid Scintillation

Issue: The accuracy and reproducibility of radionuclide measurements by liquid scintillation are

dependent on accounting for the quench (Section 15.5.3.3) of the measured test source. Quench is one of the most significant factors to be accounted for, and can be affected by solvent-to-fluor ratio, cocktail characteristics, suspension composition, acid concentration, and chemical and radiological impurities. Care must be taken to assure radionuclide purity and chemical-composition equivalence to calibration and test sources. An additional factor to consider is the ratio of sample volume to scintillation-cocktail volume (i.e., dilution factor). Although this can affect quench as well (especially if there is significant sample dilution), it is more critical that the ratios used for calibration match those in the test-source analysis.

Discussion: The process of scintillation involves the energy transfer from the emitted beta particles, slowing and stopping in the liquid medium as a result of collisions with molecularly bound electrons. The transfer of energy from the beta particle to the electrons results in solvent excitation through thermal, collisional, and photonic interactions. These excited solvent molecules transfer energy through various processes to specific organic molecules known as "fluors." The combination of the solvent and fluor is referred to as the "cocktail." The test source is the combination of the cocktail and sample.

Fluors absorb the energy and are brought to an excited state. The de-excitation of these molecules results in a photon emission that is detected by a photomultiplier tube. Many cocktail combinations contain a second fluor (referred to as a wavelength shifter) which adjusts the emitted photons to a specific bandwidth.

Any component of the cocktail that affects the energy transfer process will have a significant effect on the analysis. This effect is referred to as "quench." The quench of a cocktail can be affected by:

- Color;
- Turbidity;
- Molecules of high electron affinity;
- Solvent;
- Acidity; and
- Dissolved gases.

Quench has the effect of shifting the energy distribution of the beta particle spectrum to lower energies. Quench also can have the effect of reducing the number of net counts.

Excursions: Slowly changing liquid scintillation measurements of a sample may be due to the change in quench because of chemical attack on the cocktail system or to changes in instrument or ambient temperature during a long count. Rapid changes in liquid scintillation measurements include phase separation of the sample in the cocktail, sample precipitation, and light leaks into the instrument. Some causes of excursions in liquid scintillation analysis are listed in Table 18.4.

Examples: Specific examples of these types of excursions as it affects analysis can be seen in the examples below.

TABLE 18.4 — Some causes of excursions in liquid scintillation analysis

Physical Effects	Chemical Effects
Turbidity	Elevated concentrations of Cl^- or NO_3^-
Sample opacity or color	Solvents: $CHCl_3$, methyl ethyl ketone, CCl_4, etc.
Precipitation	Peroxide
Fingerprints on vial	Incorrect fluor
Phase separation	Expired fluor
Light leaks into instrument	Contaminated fluor
Inadequate dark adaptation	
Temperature changes	
Different vial composition	

MEASUREMENT OF ^{55}FE IN RADIOACTIVE WASTE SOLUTIONS. The separation techniques for iron generally use nitric and hydrochloric acids. Both of these acids are eliminated prior to the preparation of the cocktail by boiling down the solution with phosphoric acid. Nitric acid can decompose in room light giving rise to the gas N_2O_4, which can impart a brown color to the solution. High concentrations of chloride can act as electron scavengers in the solution. Both these conditions yield quench. Removing them with phosphoric acid maintains the solution acidity (so the iron does not precipitate) and does not act as a quench agent.

SAMPLES IN CONCENTRATED NITRIC ACID. If samples must be made with high concentrations of nitric acid, they should be measured shortly after preparation, to avoid fluor decomposition. The samples need to have their quench compared to standard samples of the same acid composition and short time following preparation.

TRITIUM IN RAINWATER. Some methods of collecting rainwater involve funneling from a large surface area (like a roof) into a collection bottle through a spout. Rainwater itself contains many contaminants, such as carbon dioxide, sulfur dioxide, and polycyclic aromatic hydrocarbons (PAHs from fossil fuel combustion), which can act as significant quench agents. Furthermore, the surface through which the water is collected may contain accumulated particulate matter that also can affect the quench. Distilling the sample would minimize the effect of their quench. Without this, the quench would be increased and the "apparent" value would have a significant uncertainty associated with it.

18.5.6 Summary Guidance on Instrument Calibration, Background, and Quality Control

Radiation detectors and nuclear instrumentation, such as spectrometry systems, should be

calibrated and maintained according to protocols and procedures documented in the laboratory's standard operating procedures and quality manual. The important calibration parameters, the performance criteria used to monitor these calibration parameters, and the frequency of re-calibrations should be addressed in these documents. Another important parameter that should be addressed is the detector background. Detector background measurements should be taken at an appropriate frequency for the purposes of determining the net count rate of a test source and for controlling contamination.

The following subsections discuss the important calibration and monitoring parameters associated with nuclear instrumentation in common use at radioanalytical laboratories. At the end of each subsection, a table provides some examples of performance criteria for the measurement parameters and the frequency of monitoring of these parameters. The information in these subsections conforms to ASTM E181, ANSI N42.12, and NELAC (2002) and uses the input of the ASTM D19.04 Subcommittee on Methods of Radiochemical Analyses for Radioactivity in Water. A few important concepts should be considered when reviewing the following sections and summary Tables 18.5 through 18.8:

- NIST-traceable radionuclide sources (or traceable to a national standards body) are to be used for all calibrations when possible (see Chapter 15, *Quantification of Radionuclides*). Sources used for QC checks do not have to be NIST-traceable.

- The frequency of performing QC detector-response measurements, or evaluating a detector background, is related to the risk (probability) that a laboratory will accept for not detecting an instrument problem or a change in background, given a certain number of samples analyzed. The acceptable risk for not detecting a problem may vary from one laboratory to another. If an instrument QC response check is performed once every 10 samples (test sources), then there is a possibility that nine samples may be counted on an instrument not meeting quality specifications before a problem is detected. Therefore, it is more appropriate to establish the frequency of instrument QC based on the number of samples processed rather than on time schedules. The examples of instrument QC frequencies presented in the following sections are considered practical for most laboratories.

- Loss of control results from a calibration performance criterion not being met, any repair or maintenance that could affect a calibration parameter, and any event (such as sudden loss of power) that could affect calibration.

- Even without loss of control, a counting or spectrometry system should be re-calibrated for test-source radionuclides, matrices, and counting geometries at a frequency consistent with specifications delineated in the laboratory's quality manual.
- For an accurate measurement of a detector's counting efficiency and resolution, as well as for a detector's QC response checks, the relative counting uncertainty (1σ) of the measurement (net count or net response) or in the individual peaks associated with spectrometry systems

should be 1 percent or less.

- Detector background measurements are used for the calculation of a net measurement response and for detector contamination control. A net measurement response is calculated using a long-duration detector background measurement in order to minimize the counting uncertainty of the measurement. Contamination control background measurements typically are taken more frequently and are of shorter duration than those for net measurement response applications. To determine possible gross contamination, the results from the contamination control background measurements should be evaluated statistically and compared to the long-duration background results.

18.5.6.1 Gas Proportional Counting Systems

CALIBRATIONS

Three parameters should be considered when calibrating a gas proportional counting system:

- Operating voltage settings on the alpha and beta voltage plateaus,
- Detector counting efficiencies, and
- Crosstalk factors.

Initially upon instrument setup, the manufacturer's specifications for these three parameters should be verified. It should be noted that the manufacturer's specifications may be based upon unique calibration sources and operating conditions that may not be similar to those used when analyzing test sources. For example, the manufacturer's detector efficiency and crosstalk factors may be based on electroplated alpha and beta sources. For most laboratories, the typical test source for GP counting is not an electroplated source, so the reference alpha and beta radionuclides for calibration are not the same as the radionuclides used by the manufacturer in developing the specifications. However, the detector's alpha and beta voltage plateau settings typically are not changed after instrument setup. The alpha and beta voltage plateau settings are selected from plots of the applied detector voltage versus the observed count rate for pure alpha and beta sources (see Chapter 15, *Quantification of Radionuclides*).

The next parameters to evaluate are the detector's alpha and beta counting efficiencies for various source geometries. Initially, the manufacturer's detector efficiency for both alpha and beta counting modes should be verified using electroplated sources. (Typical electroplated calibration sources include ^{99}Tc and ^{90}Sr for beta sources and ^{230}Th or ^{241}Am for alpha sources.) A detector's counting efficiency should be determined for each radionuclide and method used to analyze test sources. The detector efficiency should be determined for new or changed method protocols and loss of instrument control. For test sources having mass loading, an efficiency curve or mathematical function that describes the detector efficiency versus mass loading, consistent with the expected test source mass range, should be developed. For any mass in the

expected calibration range, the 95-percent confidence limits for the detection efficiency should be within 10 percent of the fitted value for alpha sources and within 5 percent of the fitted value for beta sources.

The crosstalk factors for the alpha counts into the beta channel (alpha crosstalk) and for the beta counts in the alpha channel (beta crosstalk) should be determined when applicable. The manufacturer's specifications for the crosstalk factors using electroplated sources should be verified prior to test source processing. Typical manufacturer specifications for electroplated sources are less than 1 percent alpha counts in the beta channel for ^{210}Po and less than 0.1 percent beta counts in the alpha channel for ^{90}Sr/Y. The alpha crosstalk factor will vary according to the crosstalk parameter setup, decay scheme of the alpha emitting radionuclide, and the mass (weight) of the source. Verify the manufacturer's alpha crosstalk factor using the radionuclide and crosstalk parameters setting specified by the manufacturer. The alpha crosstalk factor for other radionuclides and source masses should be determined for each method, preferably at the same time as determining the detector counting efficiency factors or efficiency versus source mass function. The crosstalk factors may be method specific and should be determined during initial calibration and after re-calibrations.

BACKGROUND

A detector's background should be determined immediately after calibration and at the instrument settings established for each method. An accurate estimate of a detector's background is needed to determine the net count rate of a source. For this application, a very long background, with respect to the nominal counting time for the test sources, typically is needed depending on the required detection limit. One approach for making long-duration background measurements is to count a clean test-source mount long enough to achieve a relative counting uncertainty (1σ) of less than 10 percent for alpha measurements and less than 3 percent for beta measurements. Alternatively, the counting time for a long-duration background measurement should be between one and four times the nominal counting duration of test sources for a given matrix and application. A long-duration background measurement should be conducted on a monthly basis. A statistical test should be used to determine if the detector's background has changed from the initial background determination.

When required, a detector may be evaluated frequently for gross contamination using a short-duration counting interval. When the counting duration of test sources is short (less than one hour), a short-duration background measurement should be conducted prior to processing test sources. When the test-source counting time is longer, the background time interval should be the same as the test sources, and the background should be determined before and after a sample (test source) batch.

CALIBRATION QC CHECKS

Once a GP counting system has been calibrated, the detector's response should be monitored frequently to determine if a significant change has occurred. Typically, a tolerance limit or control chart (Section 18.3, "Evaluation of Performance Indicators") is established to monitor the detector's response and to flag responses that exceed pre-established control limits. A tolerance limit or control chart should be established immediately after the initial counting efficiency calibration, and after instrument loss of control. A tolerance limit or control chart should be set at ± 3% or 3σ. Once a chart has been established, an instrument or detector response check should be performed after a counting-gas change and daily for short test-source counting intervals. For longer test-source counting times, a detector response check for a multi-sample shelf unit should be conducted prior to test source counting, while a detector response check for a sequential sample counter should be performed before and after the sample batch.

TABLE 18.5 — Example gas proportional instrument calibration, background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Alpha and beta plateaus and operating voltages	Prior to initial use and after loss of control.	Verify manufacturer's specifications. Plot voltage vs. count rate to determine proper operating voltages.
	Alpha and beta crosstalk factors	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings.	Verify manufacturer's specifications. Determine crosstalk factors for each nuclide, matrix and method. For mass-loaded test sources, determine crosstalk factors for the nuclide as a function of test source mass
	Detector counting efficiency	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings.	Verify manufacturer's specifications. A 1σ counting uncertainty of ≤ 1% should be achieved for all detector efficiency determinations.
	a) Weightless sources	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Recalibrate per quality manual.	Zero-mass sources using the same radio-nuclide of interest.
	b) Mass-loaded sources	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Recalibrate per quality manual.	For radionuclide of interest, establish mathematical function (curve) of detector efficiency vs. source mass loading. 95% confidence limit of the fitted function (curve) over the calibration range to ≤ 10% and ≤ 5% uncertainty for alpha and beta, respectively.
Detector Background		Determine alpha and beta background initially and after efficiency calibration.	Verify manufacturer's specifications.
a) Short count for gross contamination control	Detector background using a contamination-free source mount	Daily for short test-source counting intervals. For longer test-source counts, use the same interval as the test sources before and after a sample batch.	Use a statistical test to determine if the new background count rate is different from the initial (at time of calibration) long background count rate.

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
b) Long count for background subtraction of test sources and blanks	Detector background using a contamination-free source mount	Monthly when system is in use.	Establish a background count rate value based on measurement uncertainty or count a long background for a time interval that is 1 to 4 times the typical test-source counting time. Use statistical testing to determine a change in the long background count rate value.
Calibration QC check – detector response check	Count rate using a radionuclide source of appropriate emission and energy	Develop detector response control chart immediately after calibration and loss of control. Perform detector response check daily, prior-to-use, or bracketing a sample batch depending on test source counting time.	Count QC source to reach net 1σ counting uncertainty of ≤1%. For all detector response checks, compare performance to control chart or tolerance limits: ±3σ or ±3%.

18.5.6.2 Gamma-Ray Detectors and Spectrometry Systems

CALIBRATIONS

Three parameters should be considered when calibrating a gamma-ray (photon) detector or spectrometry system. These include the energy (gain and base) calibration, energy resolution, and the detector efficiency calibration for a particular geometry and matrix combination. Initially upon instrument setup, the manufacturer's specifications for the latter two parameters should be verified for a detector. It should be noted that verification of the manufacturer's specifications may require different instrument settings, sources, and geometries compared to those used during normal test-source analyses.

The energy calibration covers the photon energy range of the desired radionuclides expected in test sources. This calibration involves adjusting the gain of the system amplifier so that a specific slope calibration can be achieved (e.g., 0.5 keV/channel). At least two widely spaced photon peaks are needed to determine the energy calibration (Section 17.3.1, "Gamma Spectrometry"). It should be noted that verification of the manufacturer's specification for detector resolution may require a difference in energy calibration (e.g., 0.10 or 0.25 keV per channel) compared to the energy calibration settings used for typical test sources. For most modern spectrometry systems, the instrument energy parameters are very stable. The energy calibration parameter should be monitored as appropriate to support data-reduction algorithm requirements for energy fit and resolution. Typically, the determination of the energy calibration parameter can be made from the data acquired from the daily detector response QC measurement. A tolerance limit on the maximum energy calibration deviation, rather than a QC chart, can be used as an alternate to verifying amplifier output voltages. A pass-fail criterion for peak position also should be established. For example, the channel number that the ^{137}Cs 661.6 keV peak can change should be less than two channels. Some software applications adjust the energy of the gamma-ray spectrum using the daily energy calibration data. Such applications do not require changes in the settings of the

system's electronics.

The manufacturer's detector resolution, expressed as the FWHM in keV at specific photon energies, should be verified prior to use. Manufacturers of detector systems routinely establish an energy calibration of 0.25 or 0.10 keV/channel by adjusting the gain of the detection system amplifier. The FWHM and the peak-to-Compton ratio are both measured at a specified distance from the detector. Analytical laboratories frequently calibrate energies at approximately 0.50 keV/channel. Thus, prior to initial calibration or when re-calibration is necessary, the analytical laboratory should duplicate the manufacturers conditions for FWHM and peak-to-Compton ratio at the manufacturers stated initial conditions for the detector. It should be noted that the detector resolution varies with energy (Chapter 15) and can be affected by such factors as temperature, humidity, vibration, poor connectors, or poor line-voltage conditioning. The QC check sources used for the detector response check typically are used for resolution measurements during test-sources analyses. For a combined detector response and resolution check, the radionuclides selected for the QC source have photon energies that normally cover the low, middle, and high energies of the desired range (e.g., ^{241}Am, ^{137}Cs, and ^{60}Co). The photon energies selected for the resolution check should be sufficiently separated to avoid other interfering peaks. If the energy calibration settings for routine test source analyses is 0.5 keV per channel or greater, a resolution check may only indicate gross or substantial changes in a detector's resolution (e.g., greater than 10 to 20 percent). Photopeaks with greater than 10,000 counts are needed for routine resolution checks. Once the routine (operational) resolution value has been determined, limiting the maximum resolution deviation with an acceptable tolerance limit may be more suitable than using a QC chart. QC verification of resolution should be performed on a pass-fail basis. Since the FWHM varies as a function of energy, each peak should have its own acceptance criterion.

The peak-to-Compton ratio is an important characteristic of the detector that needs to be compared with the manufacturers specification upon initial detector calibration. This ensures that the maximum sensitivity for full energy peak (FEP) analysis is achieved, and the correct semiconductor crystal has been installed in the detector housing. See Section 15.6.2.1, "Detector Requirements and Characteristics," for the definition and technical basis for the peak-to-Compton ratio determination. This parameter needs to be checked during initial detector setup or prior to detector recalibration.

The next parameter that should be evaluated is the detector's efficiency response as a function of energy and matrix. The manufacturer's specification for detector efficiency is relative the efficiency of a 76 × 76 mm NaI detector responding to to ^{57}Co, ^{137}Cs, and ^{60}Co point sources at a distance of 25 cm from the detector. The standard NaI efficiency for this detector size and a ^{60}Co point source is 0.1 percent. (Gilmore and Hemingway, 1995). For each geometry/matrix combination used for test-source analyses, a gamma-ray efficiency versus energy response function (curve) must be determined. It is important that the same geometry and matrix be used for the calibration and test sources. This includes the container for these sources, as well as their physical placement relative to the detector. The efficiency check should span the energy range of

radionuclides of interest. For commercially available mixed radionuclide calibration sources, 10 data points per calibration curve is typical, covering the range of 59 keV (^{241}Am) to 1,836 (^{88}Y) keV. The 95 percent confidence limit of the fitted curve should be under 8 percent over the calibration energy region. A detector response QC chart should be established immediately after the first calibration for the detector.

DETECTOR BACKGROUND

A detector's background should be determined immediately after calibration with or without a counting container, depending on the inherent radionuclide activity levels in the counting container. An accurate estimate of a detector's background in a radionuclide photopeak is needed when determining the net photopeak count rate of a source. For this application, a very long background with respect to the nominal counting time for the test sources typically is needed, depending on the required detection limit. One approach for making long-duration background measurements is to count a clean test source mount to achieve a relative counting uncertainty (1σ) for major photopeaks that is ≤ 10 percent. Alternatively, the counting interval for the long count should be between one and four times the nominal counting interval of the test sources. A long detector background measurement should be conducted on a monthly or quarterly basis. A statistical test should be used to determine if the detector background in a photopeak has changed significantly from the initial background determination. Acceptable integrated background values will be defined by the measurement limits desired by the analytical method. The statistical criterion that constitutes a significant change should be stated in the laboratory's quality manual.

When required, the detector's background may be evaluated for gross contamination on a frequent basis using a short counting interval. Once the long background count rate has been determined, a shorter background count can be made and the results compared statistically to the long background count rate to determine possible detector contamination. For the short background, the energy region between about 50 and 2,000 keV is integrated. The counting time for the short background count should be set so that the relative counting uncertainty (1σ) of the integrated counts is ≤ 3 percent. A limit in the deviation of the integrated background value may be set using a tolerance limit or control chart. It should be verified that no extraneous peaks are identified, indicating lower-level contamination (i.e., no new peaks in the short background spectrum compared to previous spectra)

CALIBRATION QC CHECKS

After the initial detector calibration, a control chart or tolerance limit should be established (Section 18.3, "Evaluation of Performance Indicators"). Such a chart may be generated using a noncalibrated, but reproducible geometry. This source does not necessarily need to be a primary-grade calibration source, but a sealed source that is well characterized and stable. The purpose of this QC source is to validate that the detector performance is reproducible on a day-to-day basis for the detector efficiency, energy response, and resolution. These characteristics can be used on

a relative basis for the QC source as long as it is stable and sealed, so that its only change will be as the result of radioactive decay (which can be accounted for mathematically). It must cover a reasonable energy range (low, middle, and high energies), and the generated QC data should have a relative 1σ uncertainty of under 1 percent. The detector-efficiency QC response check should have a tolerance limit or control chart set at ± 3 percent or 3σ. Monitoring of gamma-ray energy resolution (as measured by the FWHM) typically is a tolerance-limit measurement. Thus, an upper bound for this value at specified energies in the calibrated range will serve as the indicator of this parameter. For example, if the acceptable limit for FWHM at the 1,332 energy peak of ^{60}Co is 2.2 keV, any value greater than 2.2 keV at this energy would cause the system to be out of tolerance. A similar situation exists for the energy QC. An upper and lower limit, based on temperature drift of the electronics and detector system, should be used as a tolerance limit. Thus, the example of the ^{60}Co peak the band of acceptable energies that the instrument measures could be from 1,331.5 to 1,333.4 keV. The small changes in parameters such as these do not significantly affect the measurement. The idea of the tolerance limit here puts a bound where an effect can indicate performance issues. It is important to note that some gamma-ray spectrometry software systems use information obtained from the daily energy QC measurement to adjust for the energy response difference when analyzing a spectrum. Any changes to the configuration, integrity or geometry of the QC standard due to age warrants an investigation of its validity.

TABLE 18.6 — Example gamma spectrometry instrument calibration, background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Detector energy calibration and high resolution peak to Compton measurements	Prior to initial use and after loss of control	Peak resolution; peak-to-Compton ratio (actual vs. manufacturer); equations for energy calibration; and shift in energy vs. channel number.
	Counting efficiency: matrix- and geometry-specific	Prior to initial use, after loss of control, and as required by quality manual.	Efficiency vs. energy for each geometry/ matrix. 95% confidence limit of the fitted function: ≤8% over energy range.
Background – Short count for controlling gross contamination	Integrate spectrum from ~50–2,000 keV	Daily or prior to use.	No extraneous peaks; tolerance limit or control chart: ± 3% or 3σ .
Background – Long count for subtracting background from blanks or test sources	Establish background peak/ region-of-interest (ROI) count rate and uncertainty for inherent radionuclides in detector, shield, and the counting geometry vessel.	Monthly or quarterly	Statistical test of successive counts and count rates for ROI show no significant difference.
Calibration QC check – Detector response	Energy, efficiency, and resolution	Daily or prior to use	Verify peak shift within tolerance limit; verify efficiency within control parameters; verify resolution in tolerance limit.

18.5.6.3 Alpha Detector and Spectrometry Systems

CALIBRATIONS

Three parameters should be considered when calibrating an alpha detector or spectrometry system. These include the energy (gain and base) calibration, energy resolution, and the detector efficiency for a particular combination of geometry and matrix. Additionally, a detector's leakage current typically is monitored to detect detector problems and possible detector-chamber light leaks. The manufacturer's specifications for detector resolution and efficiency should be verified initially upon instrument setup. Verifying the manufacturer's specifications may require different instrument settings and sources compared to those used during normal test-source analyses. The instrument setup and source geometry details normally are included in the manufacturer's documentation for a semiconductor alpha detector. The manufacturer's detector resolution (FWHM) in MeV is measured using an electroplated ^{241}Am point source in a near vacuum.

The energy calibration should be applicable to the alpha energies of the radionuclides expected in the test sources. This calibration involves adjusting the gain of the system amplifier so that a specific energy slope calibration can be achieved to cover a desired energy range. A typical energy range is between 3 and 8 MeV for long-lived radionuclides and between 3 and 10 MeV for short-lived radionuclides. At least two widely spaced alpha peaks are needed to determine the energy calibration. An energy calibration should be a linear response. However, the acceptable deviation in the energy gain (MeV per channel) depends on the total number of channels and the range of the energy spectrum.

A detector's peak counting efficiency should be determined for each test-source geometry/matrix combination that will be used. Calibration source mounts should be equivalent to the test-source mount (electroplated or microprecipitate) and have the radionuclide of interest or a radionuclide with about the same alpha energy. Most radioanalytical methods using alpha spectrometry incorporate a radioisotope tracer (radiotracer) into the sample processing scheme as a means to determine the sample-specific, chemical-yield detector-efficiency factor. For these methods, a separate detector efficiency calibration is not needed. When radiotracers are not used to determine the chemical-yield-to-detector efficiency factor, a detector should be calibrated for each test-source mounting geometry according to the frequency specified in the laboratory's quality manual. For this calibration, the peak efficiency should be determined using the average of at least two alpha peaks. When measuring a detector's counting efficiency, the source should be counted sufficiently long so that the relative uncertainty (1σ) of the alpha peak(s) count is ≤ 3 to ≤ 1 percent.

DETECTOR BACKGROUND

A detector's background should be determined immediately after detector installation, instrument setup, detector calibration, or loss of control. The background counts in an alpha peak or a region of interest for the expected radionuclides should be integrated. A blank test source mount (filter

medium or blank electroplated mount) should be counted for a time interval between one and four times the typical test-source counting time. A detector background measurement should be conducted on a monthly basis, and the results tracked. When test sources contain certain radionuclides that may contaminate the detector (see Chapter 15), a background should be taken after counting the test source. A statistical test should be applied to determine if the detector background in a photopeak or region of interest has changed compared to the initial background determination. Acceptable integrated background values will be defined by the measurement limits desired by the analytical method.

CALIBRATION QC CHECKS

When no radiotracer is used in a method, a detector efficiency determination should be performed at least monthly. The detector efficiency parameter should be recorded and evaluated for changes using a tolerance limit or control chart. The detector efficiency QC response check should have a tolerance limit or control chart set at ± 3% or 3σ. In addition, when a radiotracer is not used, a spectral energy response should be performed weekly.

Frequent use of a calibration source may lead to progressive contamination that may become significant, as a result of atom recoil from the source (Chapter 15). An electronic pulser may be used to check the spectrometry system, but not all parameters will be evaluated.

TABLE 18.7 — Example alpha spectrometry instrument calibration, background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Energy and FWHM peak resolution	Prior to initial use and after loss of control.	Verify manufacturer's specifications for alpha peak resolution and detector leakage current.
	Detector counting efficiency	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Nonradiotracer applications – calibrate per quality manual For radiotracer applications, use radiotracer with every test source.	Verify manufacturer's specifications point-source efficiency. Nonradiotracer applications, calibrate each test source mounting geometry. For radiotracer and nonradiotracer applications, 1σ relative counting uncertainty ≤ 3% to ≤ 1%.
Detector Background	Detector background – ROIs or alpha peaks	Prior to initial use or after initial calibration and monthly.	Verify manufacturer's specifications. Count a blank test -source mount (filter medium or blank electrodeposited mount) for at least 1–4 times the typical test-source counting time and determine the ROI or alpha peak background levels for background subtraction and contamination control. Track background for each radionuclide's ROI or alpha peak. Use a statistical test to determine a change in the long background count rate value for a ROI or alpha peak.

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration QC check – detector response check	Determine peak location, resolution, and ROI/alpha peak efficiency (where counting efficiency is an analytical requirement) using at least two alpha peaks.	When radiotracers are used routinely, the radiotracer can estimate the peak location, gross peak resolution, and provide the detector efficiency–chemical-yield factor. When no radiotracer is used, a detector efficiency check should be performed at least monthly and an energy check weekly.	For nonradiotracer detector response checks, use a tolerance limit or control chart: ±3% or 3σ.

18.5.6.4 Liquid Scintillation Systems

CALIBRATIONS

Following the setup of a liquid scintillation (LS) counting system, the manufacturer's specifications for counting efficiency should be verified with the appropriate reference radionuclides sources, typically unquenched LS cocktails tagged with ^{3}H and/or ^{14}C. As part of the instrument setup, the energy regions of interest (ROIs) or energy windows for the beta spectra of the radionuclides should be established. A tolerance limit or QC chart can be prepared at this time using unquenched LS standards.

The LS counting system should be calibrated specifically for a radionuclide/method application. Verify that the recommended dark-adapt time for each cocktail used in the analyses is consistent with the recommendation of the instrument or cocktail manufacturer. For method calibrations, two different approaches are taken commonly to determine the detector efficiency. These include the development of an efficiency-response/quench curve and the standard addition approach. When establishing a quench curve, a minimum of five calibration sources of different quench factors should be used, and the individual calibration sources should be counted to give a ROI relative counting uncertainty (1σ) of less than 1 percent. A mathematical function and quench curve should be developed so that the 95 percent confidence limit of the function is less than 5 percent over the expected quench range of the sources. For the standard addition approach, where a spike of the radionuclide of interest is added to a duplicate test source (or the original test source after the first analysis), the activity of the spike should be at least four times the anticipated maximum radionuclide activity in a test source. Such standard addition measurements assure that an unknown quench agent or interferent is not having an appreciable affect on the test source quench. The spiked test sources should be counted so that the ROI relative counting uncertainty is less than 3 percent. The deviation in duplicate spiked test source measurements should be evaluated statistically using the methods in Chapter 7 (*Evaluating Methods and Laboratories*) for matrix-spiked duplicates. This ensures that sample homogeneity and sample handling practices are not appreciably affecting the sample analysis.

INSTRUMENT BACKGROUND AND METHOD BLANKS

For methods that have quenched test sources, a quenched method blank (or mean of several quenched blanks) should be used to determine the background count rate that is subtracted from the count rate of the quenched test sources in a batch. A method background is determined by counting a blank sample that has been taken through the analytical process for the radionuclide of interest and determining its quench. When prepared in this manner, the blank will have a quench value similar to that of the test sources in the batch having the approximately the same quench factor. The counting interval of the blank should be the same or longer than the counting interval of test sources in the batch. Multiple quenched blank measurements should be made to establish a mean quenched-background value and standard uncertainty of the mean (standard error of the mean). These parameters should be used to determine the net count rate (and combined standard uncertainty) of test sources within a batch of samples. The ROI count rate of the quenched blank test source (processed with each batch of test sources) should be recorded and monitored. A statistical test is recommended to determine a change in the quenched background from batch to batch.

For the standard addition approach to analyzing test sources, a blank sample should be processed with each batch of samples. The counting interval of the blank should be the same or longer than the counting interval of test sources in the batch. The efficiency corrected blank activity (or mean of several batches) should be subtracted from the activities of the test sources uncorrected for chemical yield.

Longer instrument backgrounds with unquenched blank test sources may be taken for instrument-contamination control and to detect light leakage or photomultiplier tube degradation. This background measurement, which is the integral of the total energy spectrum, should be taken after initial instrument setup and monthly thereafter. The counting interval should be sufficiently long to reach an integrated spectrum count that has a relative 1σ counting uncertainty of about 1 percent. The background data should be recorded and monitored. A statistical test to determine a change in the long integrated background count rate value is recommended.

CALIBRATION QC CHECKS

Once a liquid scintillation counting system has been calibrated, the detector's response should be monitored frequently to determine if a significant change has occurred. Typically, the unquenched reference radionuclides test sources (^{3}H and/or ^{14}C) provided by the manufacturer for instrument setup are used for the QC check sources. The detector's response, measured as the integrated counts in the energy ROIs for the beta spectra of the radionuclides, should be established. A tolerance limit or control chart (Section 18.3) is used to monitor the detector's response and to reveal changes in response that exceed pre-established control limits. A tolerance limit or control chart should be established immediately after the instrument setup and after instrument loss of control. Normally, a QC source is counted to reach a relative 1σ counting

uncertainty of under 1 percent in the ROI. The detector efficiency QC response check should have a tolerance limit or control chart set at ± 3 percent or 3σ. Once a tolerance limit or control chart has been established, an instrument/detector response check should be performed before each sample batch for short test-source counting intervals, and before and after a sample batch for longer counting intervals.

TABLE 18.8 — Example liquid scintillation counting systems calibration, background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	ROI calibration with unquenched reference standards (typically ^{3}H and ^{14}C)	Prior to initial use and after loss of control and recalibrate per quality manual.	Verify sealed standards activity. Energy distribution of unquenched standard matches manufacturer's.
Method calibration (determining quenching)	Quench curve (at least five points) for each radionuclide and LS cocktail matrix.	Prior to method application, matrix, and cocktail changes. Recalibrate per quality manual.	Count individual calibration source to achieve ROI (1σ) measurement uncertainty of ≤1%. 95% confidence limit of the fitted function <5%
	Internal standard or standard addition – radionuclide of interest.	Add a spike to a duplicate processed sample or add a spike to a sample that has been counted and then recount.	Statistically evaluate replicate test-source analyses.
Background	Method background – quenched.	Each batch.	Use a statistical test to determine a change in the quenched background ROI count rate value.
	Long count background-unquenched blank.	Prior to initial use and monthly.	Monitoring of detector/ instrument contamination and electronic degradation based on integrated counts of entire spectrum.
Calibration QC Check – detector response check	ROI for unquenched reference standards (typically ^{3}H and/or ^{14}C)	Prior to use for short counting intervals. Before and after a test source batch for longer counting intervals.	Control chart or tolerance limit: ± 3σ or ± 3%.

18.5.7 Non-Nuclear Instrumentation

Radionuclides can also be measured using non-nuclear instrumentation such as mass spectrometry, fluorimetry, and phosphorimetry. These methods of analysis are discussed briefly in Chapter 15, *Quantification of Radionuclides*. Analysts can apply many of the laboratory QC techniques discussed in Sections 18.3, 18.4, and 18.6 because they are basic to any laboratory method. A quality program using statistically based control charts of the performance indicators will identify out-of-control situations, assist in improving laboratory performance, and aid in identifying the causes of trends and biases for any laboratory method. Analysts also need to

consider detection capabilities, radionuclide equilibrium, half-life, interferences, and blind samples when using non-nuclear instrumentation.

18.6 Related Concerns

18.6.1 Detection Capability

Issue: The *detection capability* of an analytical procedure is its ability to distinguish small amounts of analyte from zero (Chapter 20). The detection capability of a procedure can be estimated nominally and will depend on many factors.

Discussion: In radioanalysis, the most commonly used measure of detection capability is the minimum detectable concentration (Chapter 20). The MDC is defined as the smallest concentration of an analyte that has a specified probability of detection. The MDC is usually estimated as a nominal scoping performance measure of an analytical procedure, but a sample-specific version is reported routinely by many laboratories.

Detection capability is affected by many factors, including counting times, instrument background levels, aliquant volume, yield, decay times, and interferences. The nominal MDC is presumably based on conservative assumptions about these factors, but measurement conditions vary. The sample-specific MDC is calculated using the actual measured values of all these factors. A high MDC by itself does not indicate that a sample result is invalid or that it cannot be used for its intended purpose. However, if an analysis fails to detect the analyte of interest and the sample-specific MDC is greater than a detection limit required by contract or other agreement, it may be necessary to reanalyze the sample in a way that reduces the MDC. Such decisions should be made case-by-case, since it is not always cost-effective or even possible to reanalyze a sample, or it may not be feasible to achieve the desired MDC.

Excursions: A high sample-specific MDC can be caused by many factors, including:

- Small sample aliquant;
- Low chemical/tracer yield;
- Short counting times;
- Long decay/short ingrowth time;
- High background or blank value; and
- Low counting efficiency or sample self-attenuation.

18.6.2 Radioactive Equilibrium

Issue: It is sometimes necessary to ensure that target radionuclides are in radioactive equilibrium with their progeny, or to establish and correct for disequilibrium conditions. This is particularly

applicable for protocols that involve the chemical separation of long-lived radionuclides from their progeny. This is also applicable for nondestructive assays like gamma spectrometry where photon emission from progeny is used to determine the concentration of the non-gamma ray emitting parent (see Attachment 14A following Chapter 14 for a more thorough discussion on radioactive equilibrium).

Discussion: Some radionuclides that have long physical half-lives decay to species whose half-lives are shorter by several orders of magnitude. Following chemical separation of the parent, the progeny can "grow in" within a time frame relevant to analysis and provide measurable radioactive emissions that should be considered in the analytical method. The condition where the parent and progeny radionuclide are equal in activity is called "secular equilibrium." An example is ^{226}R, a common, naturally occurring radionuclide in the uranium series with a half-life of about 1,600 years. ^{226}Ra is found in water and soil, typically in secular equilibrium with a series of shorter-lived radionuclides that begins with the 3.8-day-half-life ^{222}Rn and ends with stable lead. As soon as ^{226}Ra is chemically separated from its progeny in an analytical procedure via coprecipitation with barium sulfate, its progeny begin to reaccumulate. The progeny exhibit a variety of alpha, beta and gamma emissions, some of which will be detected when the precipitate is counted. The activity due to the ingrowth of radon progeny should be considered when evaluating the counting data (Kirby, 1954). If counting is performed soon after chemical separation, secular equilibrium will be substantially incomplete and a sample-specific correction factor should be calculated and applied. In some cases, it may be necessary to derive correction factors for radioactive ingrowth and decay during the time the sample is counting. These factors are radionuclide specific, and should be evaluated for each analytical method.

Secular equilibrium concerns also apply to non destructive assays, particularly for uranium and thorium series radionuclides. Important radionuclides in these series (e.g., ^{238}U and ^{232}Th) have photon emissions that are weak or otherwise difficult to measure, while their shorter-lived primary, secondary or tertiary progeny are easily measured. This allows for the parents to be quantified indirectly, i.e., their concentration is determined by measuring their progeny and accounting for the amount of parent-progeny equilibrium. The amount of parent-progeny secular equilibrium is fundamental to these analyses, and data should be scrutinized to insure that the amount is valid.

When several radionuclides from one decay chain are measured in a sample, observed activity ratios can be compared to those predicted by decay and ingrowth calculations, the history of the sample and other information. For example, undisturbed soil typically contains natural uranium with approximately equal activities of ^{238}U and ^{234}U, while water samples often have very different ^{238}U/^{234}U ratio. Data from ores or materials involved in processing that could disrupt naturally occurring relationships require close attention in this regard.

All numerical protocols (electronic and manual) should be evaluated to determine if there is bias

with respect to correction factors related to equilibrium concerns. This includes a check of all constants and units used to derive such correction factors, as well as the use of input data that unambiguously state the time of all pertinent events (chemical separation and sample counting). The analyst should ensure that samples requiring progeny ingrowth are held for sufficient time before counting to establish secular equilibrium. Limits for minimum ingrowth and maximum decay times should be established for all analytical methods where they are pertinent. For ingrowth, the limits should reflect the minimum time required to ensure that the radionuclide(s) of interest has accumulated sufficiently to not adversely affect the detection limit or uncertainty. Conversely, the time for radioactive decay of the radionuclides of interest should be limited such that the decay factor does not elevate the MDC or adversely affect the measurement uncertainty. These will vary depending on the radionuclide(s) and analytical method.

Excursions: Samples where equilibrium is incorrectly assumed or calculated will produce data that do not represent the true sample concentrations. It is difficult to detect errors in equilibrium assumptions or calculations. Frequently, it takes anomalous or unanticipated results to identify these errors. In these cases, analysts need to know the sample history or characteristics before equilibrium errors can be identified and corrected. Some samples may not be amenable to nondestructive assays because their equilibrium status cannot be determined; in such cases, other analytical methods are indicated.

Examples:

Isotopic Distribution – Natural, Enriched and Depleted Uranium: Isotopic distribution is particularly important with respect to uranium, an element that is ubiquitous in nature in soils and also a contaminant in many site cleanups. The three predominant uranium isotopes of interest are ^{238}U, ^{234}U, and ^{235}U, which constitute 99.2745, 0.0055, and 0.72 atom percent, respectively, of "natural" uranium,[3] i.e., uranium as found in nature (Parrington et al., 1996). However, human activities related to uranium typically involve changing the ratio of natural uranium by separating the more readily fissionable ^{235}U from natural uranium to produce material "enriched" in ^{235}U, for use in fuel cycle and nuclear weapons related activities.[4] Typical ^{235}U enrichments range from 2 percent for commercial reactor fuels to greater than 90 percent ^{235}U for weapons. The enrichment process also produces material that is "depleted" in ^{235}U, i.e., the uranium from which the ^{235}U was taken. While the ^{235}U concentrations of depleted uranium are reduced relative to natural ores, they still can be measured by several assay techniques. This gives rise to uranium with three distinct distributions of ^{238}U, ^{235}U, and ^{234}U, referred to as "natural," "enriched," and "depleted" uranium. Because ^{238}U, ^{235}U, and

[3] The "natural abundance" of ^{235}U of 0.72 atom percent is a commonly accepted average. Actual values from specific ore samples vary.

[4] Enriched and depleted refer primarily to ^{235}U.

^{234}U are alpha emitters with considerably different physical half-lives and specific activities, a measurement of a sample's total uranium alpha activity cannot be used to quantify the sample's isotopic composition or uranium mass without knowing if the uranium is natural or has been enriched or depleted in ^{235}U. However, if this information is known, measurement and distribution of the sample's uranium alpha activity can be used to infer values for a sample's uranium mass and for the activities of the isotopes ^{238}U, ^{235}U, and ^{234}U. This ratio can be determined directly or empirically using mass or alpha spectrometry, techniques which are time and cost intensive, but which provide the material's definitive isotopic distribution. It is often practical to perform mass or alpha spectrometry on representative samples from a site to establish the material's isotopic distribution, assuming all samples from a given area are comparable in this respect. Once established, this ratio can be applied to measurements of uranium alpha activity to derive activity concentrations for ^{238}U, ^{234}U, and ^{235}U data.

18.6.3 Half-Life

Issue: Radionuclides with short half-lives relative to the time frame of the analysis may decay significantly from the time of sample collection or chemical separation to counting. In some cases, this decay will cause the ingrowth of other short-lived radionuclides. In both instances, sample-specific factors should be applied to correct the sample's observed counting/disintegration rate. Also, determination of half-life could indicate sample purity. If radioactive impurities are not appropriately corrected, analytical errors will occur. Repetitive counting of the test source may confirm the radionuclide's half-life, and thus the radioactive purity of the test source.

Discussion: When assaying for short-lived radionuclides, data should be corrected for decay over the time period between sample collection and counting. For example, operating power reactors routinely assay environmental samples for ^{131}I, a fission product with about an eight-day half-life. Samples may be counted for several days up to two weeks, during which time their ^{131}I concentration is decreasing via radioactive decay. Using the eight-day half-life, the counting data should be decay-corrected to the ending time of collection in the field and corrected for decay before and during counting. If desired, environmental samples can be decay-corrected to a time other than sample collection.

Half-life considerations also apply to radionuclide ingrowth. Certain radionuclides are assayed by an initial chemical separation, which begins a time period over which their direct progeny are allowed to reach a near-secular equilibrium condition. This is followed by additional chemical separation, purification, and counting of the progeny. The degree of the progeny's ingrowth is calculated based on the radionuclides' half-lives and the elapsed time between the two chemical separations. Allowance should also be made for the progeny's decay from separation to counting and for decay that occurred while counting, if applicable. Two examples are the beta emitting radionuclides ^{228}Ra and ^{90}Sr: they are quantified by measuring the direct progeny of each, ^{228}Ac and ^{90}Y, respectively. For airborne concentrations of ^{222}Rn, sample collection and analytical

methods should incorporate concerns related to the short-lived progeny of other radon species, such as ^{220}Rn. Other half-life related considerations apply to alpha spectrometry when assaying samples for uranium and thorium chain radionuclides. Samples that have been allowed to sit for several weeks may accumulate short-lived radionuclides that have alpha emissions whose energies are in close proximity to target radionuclides. These can interfere with quantitative analyses of the target radionuclides. Chemical yield tracers used in alpha spectrometry, such as ^{234}Th and ^{232}U, can cause this effect due to their short-lived progeny and all chemical yield tracers should be scrutinized for this potential prior to their use in analytical methods. Radionuclide specific limits for minimum ingrowth and maximum decay times should be established for all analytical methods where they are pertinent. These should be based on limiting the adverse effect of such calculations on the detection limit and measurement uncertainty. All analytical methods involving computational corrections for radioactive decay of the target species should be evaluated relative to half-life and secular equilibrium related concerns. This evaluation should be incorporated in the routine data review process that is performed on all analytical results.

A good source for radionuclide half-lives and other nuclear data can be found at the Brookhaven National Laboratory's National Nuclear Data Center (www.nndc.bnl.gov/nndc/nudat/). Using this data source will ensure consistency within and among laboratories, and will provide analysts with the current values.

Excursions: Samples that are assayed by "non destructive" techniques like gamma spectrometry may provide indications of potential complications due to half-life related considerations. Because the assay provides information on photon emitting radionuclides in the sample, the analyst can develop appropriate corrections for half-life related phenomena. However, non-spectrometric techniques like gas flow proportional counting are essentially gross counting procedures that record all events without any indication of their origin. Therefore, these data should be evaluated to ensure they are free from half-life related considerations (e.g., radionuclide purity).

Samples with short-lived radionuclide concentrations at or near environmental background will experience elevated detection limits and increased measurement uncertainty if there is excessive elapsed time between sample collection and counting. Because of the magnitude of the additional correction (decay) factor for these samples, they usually have a larger measurement uncertainty compared to longer-lived radionuclides, given equal measurement and sample conditions and parameters.

18.6.4 Interferences

Issue: Chemical or radionuclide interferences can produce erroneous results or increased measurement uncertainty.

Discussion: Analytical samples, particularly environmental samples, are often chemically complex. This complexity may include chemical constituents that interfere with an analytical method to the point that they require modification of the method. Examples of modifications include limiting the size of the sample aliquant, quantifying interfering compounds through other analyses (radiometric and non-radiometric) and changing time periods to allow adequate ingrowth of target radionuclides or decay of interferences.

A common example is groundwater or well water that contains high concentrations of salts or dissolved solids, so that screening for gross alpha activity produces erratic or anomalous results. For such samples, it may be necessary to limit the aliquant volume with the resulting increase in detection limit and measurement uncertainty. There is a salt concentration at which this procedure cannot overcome the interferences and should not be used.

Samples that contain natural concentrations of stable or radioactive compounds that are added during an analytical procedure (e.g., carrier or tracer) may also cause interference problems. Because barium is used as a carrier, water samples that contain a high concentration of barium may provide inaccurate carrier yields when screened for alpha-emitting radium isotopes. Quantifying the sample's barium content prospectively via a non-radiometric technique (e.g., atomic absorption) would be required to correct for this interference. With respect to radioactive compounds, two examples are provided. The first involves the radiochemical procedure for determining ^{228}Ra in drinking water that separates radium via coprecipitation with barium sulfate. The precipitate is allowed to come to equilibrium with its direct progeny ^{228}Ac, which is separated via co-precipitation with yttrium oxalate, purified, mounted and counted. The yttrium precipitate also carries ^{90}Y, the direct progeny of ^{90}Sr, a fission product often found in environmental samples as a result of atmospheric weapons testing and nuclear fuel cycle activities. The results of samples assayed for ^{228}Ra that contain measurable amounts of ^{90}Sr require corrections because of the differences in half-lives (^{228}Ac with a 6-hour half-life versus ^{90}Y with a half-life of about 64 hours) or other parameters. The second example involves alpha spectrometry procedures that use tracers to determine chemical yield. For example, ^{234}Th is used as a chemical yield tracer for isotopic thorium analyses. The approach assumes that the sample's inherent concentration of the tracer radionuclide is insignificant such that it will not interfere with the tracer's ability to accurately represent the sample's chemical yield. Samples that contain measurable amounts of these radionuclides may produce excessive interference and may not be amenable to this procedure.

Alpha spectra should be checked for radionuclide interferences (e.g., a ^{232}Th peak in uranium spectra). If the ^{232}Th peak is present due to incomplete chemical separation, ^{230}Th may represent interference in the ^{234}U determination. Data should be corrected or the samples reanalyzed with better target-radionuclide purification.

Each analytical method should be evaluated with respect to interferences during the method-

validation stage. Such evaluations can be based on available information and, if properly documented, can serve as the basis for developing the range of applicability, which becomes an integral part of the protocol. Evaluating performance indicators aids in the identification of samples that have interferences. All performance criteria would be protocol specific, and have clearly established acceptance ranges that incorporate the potential interferences discussed above.

Excursions: Interfering elements can affect measurement results in several ways. For example, large amounts of non-analyte elements may overload ion exchange resins, affecting the resin's ability to collect all of the analyte. In addition, spiking elements, already in the sample prior to preparation, may cause matrix spike results to exceed acceptance limits.

Carrier/tracer yields exhibiting gradual changes that appear to be correlated with a batch or group of samples from the same sampling location may indicate potentially interfering conditions. A significant decrease in the carrier/tracer yield may indicate that the analytical method is not functioning as planned. Yields that are significantly low or in excess of 100 percent may be caused by competing reactions within the sample matrix, or by the presence of an inherent carrier or tracer within the sample.

For screening analyses, e.g., gross alpha or beta, large changes in counting efficiencies or erratic counting data can reflect the presence of salts. Samples of this type are hygroscopic and continue to gain weight following preparation as they absorb moisture from the air. These changes could be detected by reweighing the planchets directly prior to counting. These samples can be converted to oxides by carefully holding them over the open flame of a laboratory burner; however, this will cause losses of volatile radionuclides, such as ^{210}Po and ^{137}Cs, which have alpha and beta emissions, respectively. An alternative approach is to thoroughly dry each planchet, record the weight and count it immediately, followed by a post-counting weighing to ensure that the weight did not change significantly over the measurement period. This approach may not be practical for all laboratories.

18.6.5 Negative Results

Issue: When an instrument background measurement is subtracted from a measurement of a low-activity sample, it is possible to obtain a net activity value less than zero.

Discussion: Many factors influence the evaluation of negative results. The simplest case occurs when the background measurement is unbiased and both the gross counts and background counts are high enough that the distribution of the net count rate is approximately normal. In this case, normal statistics can be used to determine whether a negative result indicates a problem. For example, if a sample contains zero activity, there is a very small probability of obtaining a net count rate more than two-and-a-half or three standard deviations below zero (i.e., negative value). Since the combined standard uncertainty is an estimate of the standard deviation, a result

that is less than zero by more than three times its combined standard uncertainty should be investigated. In fact, if a blank sample is analyzed using an unbiased measurement process, negative results can be expected about 50 percent of the time. As long as the magnitudes of negative values are comparable to the estimated measurement uncertainties and there is no discernible negative bias in a set of measurements, negative results should be accepted as legitimate data and their uncertainty should be assessed. On the other hand, if a sample activity value is far below zero, there may be a reason to investigate the result. A large percentage of negative results may also indicate a problem, even if all of the results are near zero. When instrument backgrounds are extremely low, statistics based on a normal distribution may not be appropriate (Chapter 19).

A preponderance of results that are negative, even if they are close to zero, indicates either a systematic error or correlations between the results. If the results are measured independently, a pattern of negative results indicates a bias, which requires investigation.

Excursions: Negative results occur routinely when samples with low levels of activity are analyzed, but a result should seldom be more than a few standard deviations below zero. Possible causes for extremely negative results or for an excessive number of negative values include:

- Instrument failure (low sample counts or high blank counts);
- Positive bias in the background or reagent blank measurement;
- Overestimation of interferences;
- Wrong or inappropriate background data;
- Data transcription error; or
- Calculation error.

18.6.6 Blind Samples

Issue: The performance of the analytical method should be assessed independently on a regular basis. This assessment is achieved through the use of blind samples that provide an objective means of evaluating the laboratory's performance when analyzing specific analytes and matrices. Blind samples can be internal or external, and either single or double. External blind performance-testing (PT) samples (also called performance-evaluation, or PE, samples) are used for QA purposes and also can provide information that is useful to laboratory QC.

Discussion: A blind sample is a sample whose concentration is not known to the analyst, and whose purpose is to assess analytical performance. Regardless of their nature, blind samples are effective only when their contents are unknown to the analysts. The preparation of all blind and other performance assessment samples is usually designated as a QA function. The QA staff functions independently from personnel responsible for sample processing and analysis. Blind samples consist of a matrix routinely processed by the laboratory that contains a known amount

of one or more analytes (radionuclides). A blind sample also may take the form of a replicate sample that is submitted for analysis such that its composition and origin are unknown to the analyst. These can be split samples (if run in the same batch) or spiked samples, and are prepared and submitted by an independent group either within the organization (internal), or from an independent organization (external). Performance on blind samples should be an integral part of the laboratory's quality system, which includes routine evaluation of their analytical results against specific performance criteria. For example, analysis of blind samples should be evaluated for relevant performance indicators. Data that fall outside an acceptance criterion may indicate loss of control in sample chemical processing, radiometric determination (counting) or other aspects of the analytical process. The ability to prepare blind samples depends fundamentally on the ability to obtain the appropriate combination of matrix with a radionuclide of a well-known concentration, ideally traceable to NIST or other appropriate certifying body. Also important are the expertise and experience of the preparer of the blind samples, proven and verified methodologies used for the blind samples, and detailed documentation. The use of blind samples assumes that their physical, chemical and radiological nature are similar to routine samples and compatible with the analytical methods employed at the laboratory.

When the analyst is aware that the sample is a blind sample but does not know the concentration, these samples are called single blinds. The analyst may know what analytes the blind sample contains, but not the analyte's concentration. Single blinds and other internal samples of this type are generally prepared by an organization's QA personnel that are independent of the samples' analyses. External single blind samples are available and can be obtained from several sources.

A double blind sample is a PT sample whose concentration and identity as a PT sample is known to the submitter but not to the analyst. The double blind sample should be treated as a routine sample by the analyst, so it is important that the double blind sample be identical in appearance to routine samples. A replicate routine sample would be considered a double blind PT sample. However, samples having sufficient measurable analyte are the most desirable as double blind samples for measuring precision. In general, a double blind is thought to be a more rigorous indication of the laboratory's performance, since analysts and other laboratory personnel may take special precautions when analyzing known PT samples, in anticipation of the greater scrutiny associated with such samples. This should not happen with double blind samples, since there should be no way to distinguish them from routine samples. However, true double blind samples are difficult to prepare.

INTERNAL BLIND SAMPLES. Internal blind samples are prepared by the laboratory's QA personnel. Internal blind samples assess several aspects of the analytical process. They allow the laboratory to demonstrate that it can successfully process routine samples for a specific analysis; in other words, they get a measured result within accepted limits. They provide an auditable, empirical record against specific quality performance criteria. They also demonstrate the efficacy of analytical methods and areas in need of adjustment. Double blind samples can pose logistical problems. It may be difficult to prepare internal double blind

samples and submit them to the laboratory for analysis successfully disguised as routine samples. Certain replicate routine samples are the exception. Evaluation criteria should be established to identify when conditions are out of acceptance limits.

EXTERNAL BLIND SAMPLES. External blind samples are those prepared by an organization outside that laboratory. This may be helpful with respect to ensuring that the analyte concentrations are truly unknown to the analyst; external blinds may offer a greater variety of matrices and analytes than can easily be produced within the laboratory and augment the laboratory's internal quality control program. Alternatively, if external blinds are not appropriate to the laboratory's programs, they will be of limited utility.

If statistical differences between observed and known values typically arise, these should be investigated thoroughly, as they indicate areas where important details of the analytical process may have been overlooked. Often a laboratory's observed values agree with the known value within acceptable tolerances, but are biased high or low. Careful documentation of the laboratory's performance in this regard can assist in characterizing the fluctuations of a measurement system or analytical method. Like other performance indicators, large or sudden changes in bias require scrutiny.

Blind samples should be an integral part of the laboratory's quality control program and they should be processed according to a predetermined schedule. Important sources of external blind samples include the NIST Radiochemistry Intercomparison Program (NRIP), National Voluntary Accreditation Program (NVLAP/EPA), Food and Drug Administration, DOE Lab Accreditation Program (DOELAP), Quality Assessment Program (DOE QAP), Multi-Analyte Performance Evaluation Program (DOE MAPEP), and several commercial vendors.

Excursions: The excursions typically encountered with analytical methods for specific parameters (carrier/tracer recovery, lack of precision, elevated backgrounds, etc.) apply to blind samples as well. Additionally, instances where the analysis of external blinds produces values that do not agree with the known values, may indicate that instrument calibrations or other correction factors require reevaluation. Problems revealed by the analysis of blind blank samples can indicate a problem (e.g., bias, blunder) within the laboratory, or conditions where the current protocol is inadequate. Excursions discovered while analyzing samples from external PT programs should be addressed.

18.6.7 Calibration of Apparatus Used for Mass and Volume Measurements

Issue: Fundamental to all quantitative analysis is the use of the proper masses and volumes. Analysts should perform careful gravimetric and volumetric measurements (especially in the preparation of calibration solutions, test sources, and reagents) in order to achieve the desired levels of precision and bias in each analytical method. Therefore, laboratory balances and

volumetric glassware and equipment should be calibrated and checked periodically to maintain the desired method performance levels. This section discusses the calibrations of laboratory balances and volumetric glassware and equipment. See Chapter 19, Attachment F, for further discussion on mass measurements.

Discussion: Laboratory balances should be periodically calibrated and checked. Most balances are typically calibrated and certified by the manufacturer once a year. These calibrations are performed to achieve the manufacturer's specified tolerances for each balance. A calibration certificate is supplied to the laboratory. In addition to this yearly calibration, daily calibration checks should be performed by the laboratory. Some laboratories check the balances once a day or at the time of each use. Any balance failing the daily calibration check should be taken out of service. Ordinarily, ASTM E617 Class 1 or 2 masses are used to perform the daily calibration check, depending on application. Over time, daily wear and tear on the masses can affect calibration, so it is a good idea to get them periodically re-certified or to purchase new masses.

Volumetric glassware and equipment, especially those used in the preparation of instrument calibration solutions and laboratory control samples, should be calibrated to the desired level of accuracy. Calibration can either be performed by the manufacturer of the equipment or by laboratory personnel. Calibration certificates for volumetric pipets and flasks are provided by the manufacturer at the time of purchase. Borosilicate and Pyrex® volumetric glassware will hold its calibration indefinitely provided that it is not exposed to hydrofluoric acid, hot phosphoric acid or strong alkalis, and that it is not heated above 150 °C when drying. Any glass volumetric pipet with a damaged tip should be discarded or re-calibrated. The manufacturer of volumetric automatic pipetting equipment calibrates the equipment and provides a certificate at the time of purchase. The re-calibration of automatic equipment should be performed annually and can be performed by the manufacturer, calibration specialty companies, or in-house laboratory personnel. Outside calibration services should provide a calibration certificate.

Laboratory personnel can calibrate and check volumetric apparatus using procedures like those specified in ASTM E542. Typically calibrations use volumes of water and are gravimetrically based. Volumes are corrected for temperature and atmospheric pressure and require thoroughly cleaned glassware, standard procedures for setting and reading the water meniscus, and accurate balances and thermometers.

Volumetric glassware is calibrated either "to contain" (TC) or "to deliver" (TD). Glassware designated as "to contain" has a mark referred to as the "fiducial mark." When the vessel is filled to that mark, it "contains" the designated volume. Emptying the vessel does not have any quantitative measure associated with it. "To deliver" glassware is not to be completely emptied or "blown out." Specified volumes for TD glassware do not include the residual left from surface adhesion and capillary action. TD glassware will perform with accuracy only when the inner surface is so scrupulously clean that the water wets it immediately and forms a uniform film when emptying.

18.7 References

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ATTACHMENT 18A
Control Charts

18A.1 Introduction

This attachment provides statistical details to augment Section 18.3.2. The term "statistical quality control" refers to QC based on statistical principles. Generally, statistical QC in the laboratory applies the principles of hypothesis testing, with varying degrees of rigor, to make inferences about a measurement system or process. The primary tool for statistical QC is the control chart.

An important reason to establish statistical QC in the laboratory is to ensure that measurement uncertainties are properly estimated. The uncertainty estimate that accompanies a measured value may be misleading unless the measurement process is in a state of *statistical control*. Statistical control implies that the distribution of measured results is stable and predictable. It exists when all the observed variability in the process is the result of random causes that are inherent in the process. The existence of variability due to "assignable" causes, including instrumental and procedural failures and human blunders, which are not inherent in the process, implies that the process is unpredictable and hence "out of control."

Statistical QC procedures are designed to detect variations due to assignable causes. When such variability is detected, specific corrective action is required to determine the cause and bring the measurement process back into a state of statistical control. Laboratory QC procedures should be definitive enough to detect variations in the measurement system that could have a significant impact on measurement uncertainties.

Statistical QC also may be used in the laboratory to monitor method performance parameters, such as chemical yield, to ensure that the measurement system is performing as expected. However, the need for corrective action in the case of a low yield may not be as urgent as in the case of a malfunctioning radiation counter, since the latter is much more likely to cause underestimation of measurement uncertainties.

The following sections describe the various types of control charts introduced in Section 18.3.2, including the X chart, $\overline{X}$ chart, R chart, and variants of the c chart and u chart for Poisson data.

18A.2 X Charts

Procedure 18.1, shown below, may be used to determine the central line, control limits, and warning limits for an X chart. Ideally, the data distribution should be approximately normal, although the X chart is often used with other types of distributions.

In order to use Procedure 18.1, an unbiased estimate of the standard deviation of the measured values $X_1, X_2, \ldots, X_n$ is required. Although the experimental variance s^2 of the data is an unbiased estimate of the true variance σ^2, taking the square root of s^2 generates a bias . The experimental standard deviation s is given by the equation

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(X_i - \overline{X})^2} \tag{18.6}$$

If the data are (approximately) normally distributed, s should then be divided by a bias-correction factor, denoted by c_4, which is determined from the number of degrees of freedom, $\nu = n - 1$, as shown in Table 18A-1 below. Thus σ is estimated by s / c_4. The factor c_4 is defined as the ratio of the expected value of the experimental standard deviation, s, to the true standard deviation, σ, and can be shown to be equal to

$$c_4 = \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right)}\sqrt{\frac{2}{n-1}} \tag{18.7}$$

where Γ denotes the *gamma function* (NBS 1964), but it is well approximated by $c_4 \approx \frac{4n-4}{4n-3}$. For large n the value of c_4 is approximately 1.

TABLE 18A.1 — Bias-correction factor for the experimental standard deviation

$\nu = n - 1$	c_4	ν	c_4	ν	c_4	ν	c_4
1	0.79788	11	0.97756	21	0.98817	31	0.99197
2	0.88623	12	0.97941	22	0.98870	32	0.99222
3	0.92132	13	0.98097	23	0.98919	33	0.99245
4	0.93999	14	0.98232	24	0.98964	34	0.99268
5	0.95153	15	0.98348	25	0.99005	35	0.99288
6	0.95937	16	0.98451	26	0.99043	36	0.99308
7	0.96503	17	0.98541	27	0.99079	37	0.99327
8	0.96931	18	0.98621	28	0.99111	38	0.99344
9	0.97266	19	0.98693	29	0.99142	39	0.99361
10	0.97535	20	0.98758	30	0.99170	40	0.99377

An alternative method of estimating the standard deviation is based on the average value of the *moving range* (ASTM D6299, ASTM E882). The moving range (MR) is the absolute value of the difference between consecutive measured values X_i and X_{i+1}. If the data are normally distributed, the expected value of the moving range is

$$\frac{2\sigma}{\sqrt{\pi}} \approx 1.128\,\sigma \tag{18.8}$$

which may be estimated by

$$\overline{\mathrm{MR}} = \frac{1}{n-1}\sum_{i=1}^{n-1}\left|X_{i+1} - X_i\right| \tag{18.9}$$

So, σ is estimated by $\overline{\mathrm{MR}} / 1.128$. The moving-range estimate of σ may be preferred because it is less sensitive to outliers in the data. Furthermore, when consecutive values of X_i are correlated, as for example when a trend is present, the moving-range estimate may produce narrower control limits, which will tend to lead to earlier corrective action.

Procedure 18.1 (X chart). Determine the central line, control limits, and warning limits for an X chart based on a series of n independent measurements, which produce the measured values $X_1, X_2, \ldots, X_n$, during a period when the measurement process is in a state of statistical control. At least 2 measurements *must* be used. Ideally, at least 20 measurements should be used.

Procedure:

1. Calculate the sum $\Sigma_{i=1}^{n} X_i$
2. Calculate the arithmetic mean $\overline{X}$ using the formula

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$$

3. Calculate an unbiased estimate $\overline{\sigma}$ of the standard deviation (e.g., s / c_4 or $\overline{\mathrm{MR}} / 1.128$)
4. Define the central line, control limits, and warning limits as follows:

$$\mathrm{CL} = \overline{X} \qquad \begin{array}{ll} \mathrm{UCL} = \overline{X} + 3\overline{\sigma} & \mathrm{LWL} = \overline{X} - 2\overline{\sigma} \\ \mathrm{LCL} = \overline{X} - 3\overline{\sigma} & \mathrm{UWL} = \overline{X} + 2\overline{\sigma} \end{array}$$

If n is less than 20, a higher rate of false warnings and failures may occur because of the increased uncertainties of the estimates $\overline{X}$ and $\overline{\sigma}$. So, fewer than 20 measured values should be used only if 20 values cannot be obtained; and the limits should be recalculated when 20 values become available.

EXAMPLE

Problem: Suppose a series of 20 observations of a parameter yield the following normally distributed values:

1,118.9	1,110.5	1,118.3	1,091.0	1,099.8	1,113.7	1,114.4	1,075.1	1,112.8	1,103.7
1,120.5	1,104.0	1,125.7	1,117.6	1,097.6	1,099.8	1,102.3	1,119.9	1,107.8	1,114.9

Determine the central line and warning and control limits for future measurements.

Solution:

Step 1 Calculate $\Sigma X_i = 22{,}168.3$

Step 2 Calculate the mean $\overline{X} = 22{,}168.3 / 20 = 1{,}108.415$

Step 3 Calculate the experimental standard deviation

$$s = \sqrt{\frac{1}{20 - 1}\sum_{i=1}^{20}(X_i - 1108.415)^2} = 12.044$$

which is based on $\nu = 19$ degrees of freedom. Find $c_4 = 0.98693$ for $\nu = 19$ in Table 18.1 (or estimate $c_4 \approx \frac{4n-4}{4n-3} = \frac{76}{77} = 0.9870$), and calculate

$$\overline{\sigma} = \frac{s}{c_4} = \frac{12.044}{0.98693} = 12.2037$$

Step 4 Define the central line, control limits, and warning limits as follows:

$$\begin{aligned} \text{CL} &= 1{,}108.415 \\ \text{UCL} &= 1{,}108.415 + 3(12.2037) = 1{,}145.0 \\ \text{LCL} &= 1{,}108.415 - 3(12.2037) = 1{,}071.8 \\ \text{UWL} &= 1{,}108.415 + 2(12.2037) = 1{,}132.8 \\ \text{LWL} &= 1{,}108.415 - 2(12.2037) = 1{,}084.0 \end{aligned}$$

18A.3 $\overline{X}$ Charts

When subgroup averages are plotted on a control chart, Steps 1 and 2 of Procedure 18.1 may be used to determine the arithmetic mean $\overline{X}$ and the standard deviation $\overline{\sigma}$ of a prior set of data $X_1, X_2, \ldots, X_n$. If k denotes the size of the subgroup, the central line, control limits, and warning limits for the subgroup average are calculated using the formulas

$$CL_{\overline{X}} = \overline{X} \qquad \begin{aligned} UCL_{\overline{X}} &= \overline{X} + 3\overline{\sigma}/\sqrt{k} \\ LCL_{\overline{X}} &= \overline{X} - 3\overline{\sigma}/\sqrt{k} \end{aligned} \qquad \begin{aligned} UWL_{\overline{X}} &= \overline{X} + 2\overline{\sigma}/\sqrt{k} \\ LWL_{\overline{X}} &= \overline{X} - 2\overline{\sigma}/\sqrt{k} \end{aligned}$$

If n is less than about 20, a higher rate of false warnings and failures may occur because of the increased uncertainties of the estimates $\overline{X}$ and $\overline{\sigma}$. For this reason fewer than 20 measured values should be used only if 20 values cannot be obtained.

EXAMPLE

Problem: Use the data from the preceding example to determine warning and control limits for subgroup averages when the subgroup size is $k = 5$.

Solution:

Step 1 Calculate $\Sigma X_i = 22{,}168.3$

Step 2 Calculate the mean $\overline{X} = 22{,}168.3 / 20 = 1{,}108.415$

Step 3 Calculate the experimental standard deviation

$$s = \sqrt{\frac{1}{20-1}\sum_{i=1}^{20}(X_i - 1108.415)^2} = 12.044$$

which is based on $\nu = 19$ degrees of freedom. Find $c_4 = 0.98693$ for $\nu = 19$ in Table 18A-1 (or estimate $c_4 \approx \frac{4n-4}{4n-3} = \frac{76}{77} = 0.9870$), and calculate

$$\overline{\sigma} = \frac{s}{c_4} = \frac{12.044}{0.98693} = 12.2037$$

Step 4 Define the central line, control limits, and warning limits as follows:

$$\begin{aligned} CL_{\overline{X}} &= 1{,}108.415 \\ LCL_{\overline{X}} &= 1{,}108.415 - 3(12.2037)/\sqrt{5} = 1{,}092.0 \\ UCL_{\overline{X}} &= 1{,}108.415 + 3(12.2037)/\sqrt{5} = 1{,}124.8 \\ LWL_{\overline{X}} &= 1{,}108.415 - 2(12.2037)/\sqrt{5} = 1{,}097.5 \\ UWL_{\overline{X}} &= 1{,}108.415 + 2(12.2037)/\sqrt{5} = 1{,}119.3 \end{aligned}$$

18A.4 *R* Charts

The *range* of a set of values is defined as the difference between the largest value and the smallest value in the set. When data are collected in subgroups, as described above, the range of each subgroup may be plotted on a *range chart*, or *R chart*, to monitor within-group variability.

The central line for an R chart can be obtained by averaging the observed ranges for a series of subgroups. Then the upper control limit for the chart can be obtained by multiplying the average range, $\overline{R}$, by a factor, denoted by D_4, whose value depends on the subgroup size, N. When $N \geq 7$, there is another factor, D_3, by which $\overline{R}$ can be multiplied to give the lower control limit. When $N < 7$, the R chart has no lower control limit. Values for D_3 and D_4 are tabulated in *Manual on Presentation of Data and Control Chart Analysis* (ASTM MNL7), as well as many other references.

For example, if an analyst makes a series of duplicate measurements of some quantity ($N = 2$), the central line of the R chart equals the average of the measured ranges, $\overline{R}$; the upper control limit equals the product of $\overline{R}$ and the factor D_4, whose value is 3.267 for duplicate measurements. The steps for calculating the central line and upper control limit when $N = 2$ are shown explicitly in Procedure 18.2 below.

Procedure 18.2 (*R* chart). Determine the central line and control limits for a R chart based on a series of n independent sets of duplicate measurements, which produce the values $R_1, R_2, \ldots, R_n$, during a period when the measurement process is in a state of statistical control.

Procedure:

1. Calculate the range, R_i, of each pair of duplicate measurements, (x_i, y_i)

$$R_i = |x_i - y_i|$$

2. Calculate the mean range, $\overline{R}$, using the formula

$$\overline{R} = \frac{1}{n} \sum_{i=1}^{n} R_i$$

3. Calculate the upper control limit as UCL = 3.267 $\overline{R}$

This approach may also be used for the moving range of a series of individual results.

EXAMPLE

Problem: Suppose a series of 20 duplicate observations of a parameter yield the following pairs of values.

(0.501, 0.491)	(0.490, 0.490)	(0.479, 0.482)	(0.520, 0.512)	(0.500, 0.490)
(0.510, 0.488)	(0.505, 0.500)	(0.475, 0.493)	(0.500, 0.515)	(0.498, 0.501)
(0.523, 0.516)	(0.500, 0.512)	(0.513, 0.503)	(0.512, 0.497)	(0.502, 0.500)
(0.506, 0.508)	(0.485, 0.503)	(0.484, 0.487)	(0.512, 0.495)	(0.509, 0.500)

Determine the central line and upper control limit for the range of future pairs of measurements.

Solution:

Step 1 Calculate the range of each of the 20 pairs:

0.010	0.000	0.003	0.008	0.010
0.022	0.005	0.018	0.015	0.003
0.007	0.012	0.010	0.015	0.002
0.002	0.018	0.003	0.017	0.009

Step 2 Calculate the mean range $\overline{R} = \frac{1}{20}\sum_{i=1}^{20} R_i = \frac{0.189}{20} = 0.00945$

Step 3 Calculate the upper control limit: UCL = 3.267 $\overline{R}$ = (3.267)(0.00945) = 0.0309

18A.5 Control Charts for Instrument Response

A radioactive check source should be used to monitor the radiation response/efficiency of every radiation counting instrument. MARLAP recommends that the activity and count time for the source be chosen to give no more than 1 percent counting uncertainty (ANSI N42.23). In other words, at least 10,000 counts should be obtained in each measurement of the source. There may be cases when placing a high-activity source in a detector is undesirable, so obtaining 10,000 counts is impractical.

The instrument response may not have a Poisson distribution. In this case, if the check source is long-lived, an X or $\overline{X}$ chart based on replicate measurements should be set up. For example, an X or $\overline{X}$ chart is the appropriate radiation response/efficiency chart for a high-purity germanium detector when the area of a specific photopeak is monitored, since the calculated size of the photopeak may have significant sources of uncertainty in addition to counting uncertainty. An X or $\overline{X}$ chart may be used even if the response is truly Poisson, since the Poisson distribution in this case is approximated well by a normal distribution, but slightly better warning and control limits are obtained by using the unique properties of the Poisson distribution.

Standard guidance documents recommend two types of control charts for Poisson data. A "*c* chart" typically is used in industrial quality control to monitor the number of manufacturing defects per item. A "*u* chart" is used to monitor the number of defects per unit "area of opportunity," when the area of opportunity may vary. Thus, the values plotted on a *c* chart are counts and those plotted on a *u* chart are count rates. The same two types of charts may be adapted for monitoring counts and count rates produced by a radioactive check source. When a *u* chart is used, the "area of opportunity" equals the product of the count time and the source decay factor. In radiation laboratories a variant of the *u* chart is more often used when the count time remains fixed but the decay factor changes during the time when the chart is in use.

Before using control limits derived from the Poisson model, one should use Procedure E1, described in Section 18B.2 of Attachment 18B, to confirm experimentally that the Poisson approximation is adequate and that any excess variance is relatively small at the expected count rate. Factors such as source position that may vary during routine QC measurements should be varied to the same degree during the experiment.

Calculation of warning and control limits using the Poisson model requires only a precise measurement of the source at a time when the instrument is operating properly at the time of calibration. The precision can be improved either by counting the source longer or by averaging several measurements. In principle both approaches should provide equally good estimates of the count rate; however, an advantage of the latter approach is that it can provide the data needed to detect excess variance (using Procedure E1).

Procedures 18.2 and 18.3, listed below, may be used to determine warning and control limits for measurements of a radioactive check source when the total count follows the Poisson model. Procedure 18.2 is for control charts and should be used only when the expected count in each measurement is the same, for example when the source is long-lived and all count durations are equal. Procedure 18.3, which implements an alternative to the *u* chart, may be used in all other cases.

Procedure 18.2 (Control chart for Poisson efficiency check data with constant mean). A check source is counted n times on an instrument, producing the measured counts $N_1, N_2, \ldots, N_n$. (Ideally, n is at least 20.) Determine control limits and warning limits for future measurements of the source count on the same instrument.

Procedure:

1. Estimate the central line by

$$\mathrm{CL} = \frac{1}{n}\sum_{i=1}^{n} N_i$$

and the standard deviation by

$$s = \sqrt{CL}$$

NOTE: The estimate s is biased, but the bias is negligible for the large number of counts typically obtained from a check source.

2. Define the control limits and warning limits (in counts) as follows:

$$UCL = CL + 3s \qquad UWL = CL + 2s$$
$$LCL = CL - 3s \qquad LWL = CL - 2s$$

If n is less than 20, a higher rate of false warnings and failures may occur because of the uncertainty in the estimate of the mean. So, fewer than 20 measurements should be used only if 20 measured values are not available.

Procedure 18.3 (Control chart for Poisson efficiency check data with variable mean). A check source is counted n times ($n \geq 1$) on an instrument, producing the measured counts N_1, N_2, ..., N_n. (It is assumed that the background level is negligible when compared to the source count rate.) Let t_i denote the duration of the i^{th} measurement and d_i the decay factor [for example, $\exp(-\lambda(\Delta t + 0.5t_i))$]. Determine control limits and warning limits for a future measurement of the source count on the same instrument when the counting period is T and the decay factor is D.

Procedure:

1. Compute the sums $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} t_i d_i$.
2. Estimate the mean decay-corrected count rate by

$$\hat{r} = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} t_i d_i}$$

3. Estimate the central line by

$$CL = \hat{r}TD$$

and the standard deviation s by

$$s = \sqrt{CL}$$

4. Define the control limits and warning limits as follows:

$$\text{UCL} = \text{CL} + 3s \qquad \text{UWL} = \text{CL} + 2s$$
$$\text{LCL} = \text{CL} - 3s \qquad \text{LWL} = \text{CL} - 2s$$

If $\Sigma t_i d_i < 20\,TD$, a higher rate of false warnings and failures may occur because of increased uncertainty in the estimate of the count rate $\hat{r}$.

EXAMPLE

Problem: A source containing ^{90}Sr and ^{90}Y in equilibrium is used for efficiency checks on a proportional counter. Near the time of calibration, a series of twenty 600-s measurements are made. The observed counts are as follows:

12,262	12,561	12,606	12,381	12,394	12,518	12,399	12,556	12,565	12,444
12,432	12,723	12,514	12,389	12,383	12,492	12,521	12,619	12,397	12,562

Assume all twenty measurements are made approximately at time 0, so the ten decay factors d_i are all equal to 1. Use Procedure 18.3 to calculate lower and upper control limits for a 600-s measurement of the same source at a time exactly 1 year later.

Solution:

Step 1 Compute the sums $\Sigma N_i = 249{,}718$ and $\Sigma t_i d_i = 12{,}000$.

Step 2 Calculate $\hat{r} = \dfrac{\Sigma N_i}{\Sigma t_i d_i} = \dfrac{249{,}718}{12{,}000} = 20.80983$

Step 3 The decay time for the final measurement is 1 y = 31,557,600 s. The corresponding decay factor is $D = 0.976055$. The count time is $T = 600$ s. So, compute

$$\text{CL} = (20.80983)(600)(0.976055) = 12{,}187$$

and

$$s = \sqrt{12{,}187} = 110.39$$

Step 4 The control limits and warning limits are

$$\text{UCL} = 12{,}187 + 3 \times 110.39 = 12{,}518$$
$$\text{LCL} = 12{,}187 - 3 \times 110.39 = 11{,}856$$
$$\text{UWL} = 12{,}187 + 2 \times 110.39 = 12{,}408$$
$$\text{LWL} = 12{,}187 - 2 \times 110.39 = 11{,}966$$

If substantial excess (non-Poisson) variance is present in the data, the simple Poisson charts described above should not be used. The *c* chart may be replaced by an X chart or $\overline{X}$ chart, but a new type of chart is needed to replace the *u* chart. To determine warning and control limits for this chart, one must determine the relative excess variance of the data ξ^2. A value of ξ^2 may be assumed or it may be estimated using procedures described in Attachment 18B. Then Procedure 18.3 may be replaced by the Procedure 18.4, shown below.

Procedure 18.4 (Control chart for Poisson efficiency check data with excess variance). A check source is counted n times on an instrument, producing the measured counts $N_1, N_2, \ldots, N_n$. Let t_i denote the duration of the i^{th} measurement and d_i the decay factor. Let the data follow an approximately Poisson distribution with relative excess variance ξ^2. Determine control limits and warning limits for a future measurement of the source count on the same instrument when the counting period is T and the decay factor is D.

Procedure:

1. Compute the sums $\Sigma_{i=1}^{n} N_i$ and $\Sigma_{i=1}^{n} t_i d_i$
2. Estimate the mean decay-corrected count rate $\hat{r}$ by

$$\hat{r} = \frac{\sum_{i=1}^{n} \frac{N_i}{1 + r_0 t_i d_i \xi^2}}{\sum_{i=1}^{n} \frac{1}{1 + r_0 t_i d_i \xi^2}} \qquad \text{where} \qquad r_0 = \frac{\Sigma_{i=1}^{n} N_i}{\Sigma_{i=1}^{n} t_i d_i}$$

3. Estimate the central line by

$$\text{CL} = \hat{r} T D$$

and the standard deviation s by

$$s = \sqrt{\text{CL} + \xi^2 \text{CL}^2}$$

4. Define the control limits and warning limits as follows:

$$\text{UCL} = \text{CL} + 3s \qquad \text{UWL} = \text{CL} + 2s$$
$$\text{LCL} = \text{CL} - 3s \qquad \text{LWL} = \text{CL} - 2s$$

18A.6 References

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ATTACHMENT 18B
Statistical Tests for QC Results

18B.1 Introduction

Attachment 18A describes several types of control charts that may be used for statistical quality control in the laboratory. This attachment describes additional statistical methods that may be used, where appropriate, to test the performance of measurement results from blank, replicate, LCS, spikes, CRM, yield-monitor, background, efficiency, calibration, or peak resolution results, with special emphasis on instrumentation results.

18B.2 Tests for Excess Variance in the Instrument Response

As noted in Chapter 19, the counting uncertainty given by the Poisson approximation does not describe the total variability in a counting measurement. A number of factors may generate a small excess component of variance. When a large number of counts are obtained in the measurement, the relative magnitude of the Poisson variance is small; so, the excess component may dominate.

Regardless of whether replication or the Poisson approximation is used to estimate counting uncertainties, MARLAP recommends that a series of check source measurements be made on each instrument periodically to test for excess variance. Procedure E1, which is presented below, may be used to evaluate the measurement results. To check the stability of the instrument itself, one should perform the measurements while holding constant any controllable factors, such as source position, that might increase the variance. To check the variance when such factors are not constant, one may use Procedure E1 but vary the factors randomly for each measurement.

Assume n measurements of the source produce the counts $N_1, N_2, \ldots, N_n$. If the expected count for each measurement is at least 20, so that the Poisson distribution is approximated by a normal distribution, and if the average decay-corrected count rate $\hat{r}$ is determined with adequate precision, then the quantity

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i d_i} - \hat{r} \right)^2 t_i d_i \qquad (18.10)$$

where t_i and d_i are the count time and source decay factor for the i^{th} measurement, respectively, should be distributed approximately as chi-square with $n - 1$ degrees of freedom.[5] The precision

[5] If r denotes the true mean decay-corrected count rate, then under the null hypothesis each measured count rate $N_i / t_i d_i$ is approximately normal with mean r and variance $r / t_i d_i$, and the least-squares estimator for r is $\hat{r} = \Sigma N_i / \Sigma t_i d_i$. So, the sum $\Sigma (N_i / t_i d_i - \hat{r})^2 / (r / t_i d_i)$ is approximately chi-square with $n - 1$ degrees of freedom.

of the estimate $\hat{r}$ should be adequate for the test as long as the expected count for each measurement is at least 20. Since a check source is involved, the expected count is usually much greater than 20.

Procedure E1. The χ^2 (chi-square) analysis can be used to determine whether a series of measurements of a check source provide evidence of variance in excess of the Poisson counting variance. Let N_i denote the count observed in the i^{th} measurement. Let $w_i = t_i d_i$, where t_i denotes the count time and d_i denotes the source decay factor (if relevant). If all the values w_i are equal, one may use $w_i = 1$ instead for all i. It is assumed either that the background count rate is negligible or that the decay factors are all nearly equal, so that the expected count in each measurement is proportional to w_i.[6] The procedure tests the null hypothesis that the total measurement variance is the Poisson counting variance.

Procedure:

1. Choose the significance level α
2. Calculate the sums $\Sigma_{i=1}^{n} N_i$ and $\Sigma_{i=1}^{n} w_i$
3. Estimate the mean decay-corrected count rate by

$$\hat{r} = \frac{\Sigma_{i=1}^{n} N_i}{\Sigma_{i=1}^{n} w_i} \tag{18.11}$$

4. Calculate the chi-square statistic as follows:

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{w_i} - \hat{r} \right)^2 w_i \tag{18.12}$$

5. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.3 in Appendix G). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi^2_{1-\alpha}(n-1)$. In this case conclude that the variance is greater than predicted by the Poisson model.

If $\hat{r}$ is determined accurately, the true mean count rate r may be replaced in the formula by its estimated value $\hat{r}$ to obtain the formula that appears in the text. If all the products $t_i d_i$ are equal, they cancel out of the sum, which becomes $\Sigma(N_i - \overline{N})^2 / \overline{N}$, as described by Evans (1955), Goldin (1984), and Knoll (1989).

[6] The expected gross count for the i^{th} measurement equals $R_B t_i + r w_i$, where r is the mean net count rate at time 0. The expected count is proportional to w_i if $R_B = 0$, or if all the decay factors are equal so that $t_i \propto w_i$.

EXAMPLE

Problem: A long-lived source is counted $n = 20$ times in a gross radiation detector and the duration of each measurement is 300 s. The following total counts are measured:

11,189	11,105	11,183	10,910	10,998	11,137	11,144	10,751	11,128	11,037
11,205	11,040	11,257	11,176	10,976	10,998	11,023	11,199	11,078	11,149

Are these data consistent with the assumption that the measurement variance is no greater than predicted by the Poisson model? Use 5 percent as the significance level.

Solution:

Step 1 The significance level is specified to be $\alpha = 0.05$

Step 2 Since the source is long-lived and all the count times are equal, let $w_i = 1$ for each i. Calculate $\Sigma N_i = 221{,}683$ and $\Sigma w_i = 20$

Step 3 Calculate the mean count rate $\hat{r} = 221{,}683 / 20 = 11{,}084.15$

Step 4 Calculate the chi-square statistic

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{w_i} - \hat{r} \right)^2 w_i = \frac{1}{11{,}084.15} \sum_{i=1}^{20} (N_i - 11{,}084.15)^2 = 24.87$$

Step 5 The number of degrees of freedom is $20 - 1 = 19$. According to Table G.3, the 0.95-quantile for a chi-square distribution with 19 degrees of freedom is 30.14. Since $24.87 \leq 30.14$, do not reject the null hypothesis. The data are consistent with the assumption of Poisson counting statistics at the 5 percent significance level.

A two-sided version of Procedure E1 may also be used to test whether the measurement variance is either greater than or less than predicted by the Poisson model. Step 5 must be changed so that the null hypothesis is rejected if the value of the test statistic χ^2 does not lie between the two quantiles $\chi^2_{\alpha/2}(n - 1)$ and $\chi^2_{1-\alpha/2}(n - 1)$.

A chi-square test may require many measurements or long count times to detect a small excess variance component. When all measurements have the same expected count μ, the detection limit for the *relative* excess variance, or its minimum detectable value, is equal to

$$\xi_D^2 = \frac{1}{\mu} \left(\frac{\chi^2_{1-\alpha}(n-1)}{\chi^2_{\beta}(n-1)} - 1 \right) \tag{18.13}$$

where β is the specified probability of a type II error (failure to detect) (Currie,1972). Note that since ξ_D^2 represents a relative variance, its square root ξ_D represents a relative standard deviation.

EXAMPLE: A long-lived source is counted 20 times, and each measurement has the same duration. The average of the measured counts is 10,816. If $\alpha = \beta = 0.05$, the minimum detectable value of the relative excess variance is estimated by

$$\xi_D^2 = \frac{1}{10{,}816}\left(\frac{\chi^2_{0.95}(19)}{\chi^2_{0.05}(19)} - 1\right) = \frac{1}{10{,}816}\left(\frac{30.14}{10.12} - 1\right) = \frac{1.978}{10{,}816} = 1.829 \times 10^{-4}$$

which corresponds to a relative standard deviation $\xi_D = \sqrt{1.829 \times 10^{-4}} = 0.01352$, or about 1.35 percent.

If (1) the relative excess variance in a measurement is not affected by count time, (2) a fixed total count time is available, and (3) all measurements have the same expected count (e.g., when all count times are equal and the source is long-lived), then it is possible to determine the number of measurements that minimizes ξ_D^2 (Currie, 1972). The optimal number is the number n that minimizes the quantity

$$F(n) = n\left(\frac{\chi^2_{1-\alpha}(n-1)}{\chi^2_{\beta}(n-1)} - 1\right) \tag{18.14}$$

The solution may be found by computing $F(n)$ for $n = 2, 3, 4, \ldots$, until the computed value begins to increase. When $\alpha = \beta = 0.05$, the optimal number of measurements is $n = 15$, although the improvement as n increases from 6 to 15 is slight. If n is increased further, the detection limit ξ_D^2 worsens unless the total count time is also increased.

A chi-square test may also be used to test whether the total source measurement variance consists of a Poisson component and a specified excess component (Currie 1972). Procedure E2, described below, implements this test. If the specified component is zero, Procedure E2 is equivalent to E1.

Procedure E2. Determine whether a series of measurements of a check source provide evidence that the measurement variance is greater than the Poisson component plus a specified excess component. (Refer to the notation used in Procedure E1.) Let ξ^2 denote the value of the relative excess variance under the null hypothesis H_0.

Procedure:

1. Choose the significance level α.

2. Calculate the sums $\Sigma_{i=1}^{n} N_i$ and $\Sigma_{i=1}^{n} w_i$, where $N_1, N_2, \ldots, N_n$ are the measured values.

3. Estimate the mean decay-corrected count rate $\hat{r}$ in two steps by

$$r_0 = \frac{\Sigma_{i=1}^{n} N_i}{\Sigma_{i=1}^{n} w_i} \qquad \text{and} \qquad \hat{r} = \sum_{i=1}^{n} \frac{N_i}{1 + r_0 w_i \xi^2} \Big/ \sum_{i=1}^{n} \frac{w_i}{1 + r_0 w_i \xi^2} \tag{18.15}$$

   (If $w_1 = w_2 = \cdots = w_n$ or $\xi^2 = 0$, then $\hat{r} = r_0$.)

4. Calculate the chi-square statistic as follows:[7]

$$\chi^2 = \sum_{i=1}^{n} \frac{(N_i / w_i - \hat{r})^2}{\hat{r} / w_i + \hat{r}^2 \xi^2} \tag{18.16}$$

5. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.3). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi^2_{1-\alpha}(n-1)$. In this case conclude that the relative excess variance is greater than ξ^2.

Procedure E2, like E1, can easily be converted to a two-sided test by changing Step 5.

The excess component may be estimated by solving Equations 18.15 and 18.16 for the value of ξ that gives $\chi^2 = n - 1$. An iterative computer algorithm, such as bisection, which repeatedly tries values of ξ and computes χ^2 can be used.[8] An approximate confidence interval for the relative excess variance may similarly be found by solving for values of ξ which give $\chi^2 = \chi^2_{(1\pm\gamma)/2}(n-1)$, where γ is the desired confidence coefficient (Currie, 1972).

If $w_1 = w_2 = \cdots = w_n$, the iterative algorithm is unnecessary. In this case the value of ξ may be estimated directly using the formula

[7] In Currie (1972), the variance of N_i is estimated by $N_i + \xi^2 N_i^2$. The estimated variance used here is calculated by pooling the counting data to reduce any small bias caused by the correlation between N_i and $N_i + \xi^2 N_i^2$.

[8] Newton's method, which converges more rapidly, can also be used, but its use is more practical if one replaces $\hat{r}$ by r_0 in the denominator of each term of Equation 18.16.

$$\xi^2 = \frac{1}{\overline{N}^2}\left(\frac{1}{n-1}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.17}$$

or by $\xi = 0$ if the preceding formula gives a negative result. Similarly, the approximate lower confidence limit is given by the formula

$$\xi^2_{\text{lower}} = \frac{1}{\overline{N}^2}\left(\frac{1}{\chi^2_{(1+\gamma)/2}(n-1)}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.18}$$

and the approximate upper confidence limit is given by

$$\xi^2_{\text{upper}} = \frac{1}{\overline{N}^2}\left(\frac{1}{\chi^2_{(1-\gamma)/2}(n-1)}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.19}$$

EXAMPLE

Problem: A long-lived efficiency check source is counted once a day for 20 days, and each measurement has the same duration. Suppose the measured counts (N_i) are:

14,454	15,140	15,242	14,728	14,756	15,040	14,768	15,128	15,150	14,872
14,845	15,511	15,032	14,746	14,731	14,982	15,047	15,272	14,765	15,143

Use these data to estimate ξ and determine a 95 percent two-sided confidence interval for its value.

Solution: Since the source is long-lived and all the measurements have the same duration, $w_1 = w_2 = \cdots = w_{20}$ and Equations 18.17 through 18.19 may be used. So, calculate $\Sigma N_i = 299{,}352$ and $\overline{N} = 299{,}352 / 20 = 14{,}967.6$. Then the value of ξ is estimated as

$$\xi = \frac{1}{14{,}967.6}\sqrt{\frac{1}{20-1}\sum_{i=1}^{20}(N_i - 14{,}967.6)^2 - 14{,}967.6} = 0.014463$$

The 95 percent confidence limits are calculated as follows:

$$\xi_{lower} = \frac{1}{\overline{N}}\sqrt{\frac{1}{\chi^2_{0.975}(20-1)}\sum_{i=1}^{20}(N_i - \overline{N})^2 - \overline{N}}$$

$$= \frac{1}{14{,}967.6}\sqrt{\frac{1}{32.852}\sum_{i=1}^{20}(N_i - 14{,}967.6)^2 - 14{,}967.6}$$

$$= 0.0096334$$

$$\xi_{upper} = \frac{1}{\overline{N}}\sqrt{\frac{1}{\chi^2_{0.025}(20-1)}\sum_{i=1}^{20}(N_i - \overline{N})^2 - \overline{N}}$$

$$= \frac{1}{14{,}967.6}\sqrt{\frac{1}{8.9065}\sum_{i=1}^{20}(N_i - 14{,}967.6)^2 - 14{,}967.6}$$

$$= 0.022846$$

For most practical purposes the excess variance may be considered negligible in a counting measurement if the total count N is less than $1 / 10\xi^2$, since, in this case, the excess variance increases the standard deviation of the measured count by less then 5 percent. Similarly, the counting variance may be considered negligible if $N \geq 10 / \xi^2$.

EXAMPLE: Suppose $N = 1{,}000$ counts observed in a measurement and ξ has been estimated to be 0.01. Then $N = 1 / 10\xi^2$. The standard uncertainty of N is evaluated as

$$u(N) = \sqrt{N + \xi^2 N^2} = \sqrt{1{,}000 + 10^{-4}10^6} = \sqrt{1{,}100} \approx 1.05\sqrt{N}$$

If $N = 100{,}000$, then $N = 10 / \xi^2$ and

$$u(N) = \sqrt{10^5 + 10^{-4}10^{10}} = \sqrt{1{,}100{,}000} \approx 1.05(\xi N)$$

So, $u(N) \approx \sqrt{N}$ for $N \leq 1{,}000$, and $u(N) \approx \xi N$ for $N \geq 100{,}000$.

18B.3 Instrument Background Measurements

This section presents statistical tests related to measurements of instrument background levels. The tests are intended for single-channel detectors but may be applied to multichannel systems if wide spectral regions are integrated. Tests are described for comparing background levels to preset limits, for detecting changes in background levels between measurements, and for detecting the presence of variability in excess of that predicted by the Poisson model.

Each of the statistical tests in this section includes different instructions depending on whether the number of background counts in a measurement is at least 20. The reason for this is that when the expected number of counts is high enough, the Poisson distribution can be approximated by a normal distribution, which simplifies the test procedure. For more information about the Poisson distribution and the normal approximation, see Section 19A.2.9, "Poisson Distributions."

18B.3.1 Detection of Background Variability

The chi-square test (Procedure E1) used to detect excess variance in measurements of a check source may be adapted for background measurements. Procedure B1 implements a chi-square test for backgrounds. This test is one-sided, although Step 6 can be modified to implement a two-sided test.

Procedure B1. Determine whether a series of measurements of an instrument's background provide evidence of variance in excess of the Poisson counting variance. Let N_i denote the count observed in the i^{th} measurement, and let t_i denote the count time.

Procedure:

1. Determine the significance level α
2. Calculate the sums $\Sigma_{i=1}^{n} N_i$ and $\Sigma_{i=1}^{n} t_i$
3. Estimate the mean background count rate by

$$\hat{r} = \frac{\Sigma_{i=1}^{n} N_i}{\Sigma_{i=1}^{n} t_i} \qquad (18.20)$$

4. Let t_{min} be the smallest value of t_i. If $\hat{r}\, t_{min} \geq 20$, go to Step 5. Otherwise, discard all measured values N_i for which $\hat{r}\, t_i < 20$. If possible, restart the test at Step 2; if not, stop.

5. Calculate the chi-square statistic as follows:

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i} - \hat{r} \right)^2 t_i \qquad (18.21)$$

6. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.3 in Appendix G). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi^2_{1-\alpha}(n-1)$. In this case, conclude that the instrument background does not follow the Poisson model.

EXAMPLE

Problem: Twenty overnight background measurements are performed on a proportional counter. The duration of each measurement is 60,000 s, and the following alpha counts are measured:

14	23	23	25	28	22	19	26	20	27
30	21	34	32	24	27	25	19	19	25

Are these data consistent with the assumption that the measurement variance is attributable to Poisson counting statistics? Use 5 percent as the significance level.

Solution:

Step 1 The significance level is specified to be $\alpha = 0.05$

Step 2 Calculate $\Sigma N_i = 483$ and $\Sigma t_i = 20 \times 60{,}000 = 1{,}200{,}000$

Step 3 Calculate the mean count rate $\hat{r} = 483/1{,}200{,}000 = 0.0004025$

Step 4 Since $t_{min} = 60{,}000$, $\hat{r}t_{min} = 24.15$. Since $24.15 \geq 20$, go to Step 5

Step 5 Calculate the chi-square statistic

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i} - \hat{r} \right)^2 t_i = \frac{1}{0.0004025} \sum_{i=1}^{20} \left(\frac{N_i}{60{,}000} - 0.0004025 \right)^2 60{,}000 = 18.49$$

Step 6 The number of degrees of freedom is $20 - 1 = 19$. According to Table G.3, the 0.95-quantile for a chi-square distribution with 19 degrees of freedom is 30.14. Since $18.49 \leq 30.14$, do not reject the null hypothesis. The data are consistent with the Poisson model.

All the background tests described below are based on the assumption of Poisson counting statistics. If Procedure B1 indicates the Poisson assumption is invalid, each test requires modification or replacement. In most cases, unless the observed background counts are very low, standard statistical tests for normally distributed data may be used instead (e.g., NBS, 1963; EPA, 2000).

18B.3.2 Comparing a Single Observation to Preset Limits

High background levels on an instrument degrade detection capabilities and may indicate the presence of contamination. Unusually low levels on certain types of instruments may indicate instrument failure. When these issues are of concern, one or both of the two statistical tests described below may be performed to determine whether the true background level is outside of its desired range.

The result of the background measurement in counts is assumed to have a Poisson distribution. In both of the following tests, t denotes the count time, and r denotes the preset lower or upper limit for the true mean background count rate R_B. Given an observed count N_B, Procedure B2 determines whether $R_B > r$ and B3 determines whether $R_B < r$.

Procedure B2 should be used when r is an upper limit and B3 should be used when r is a lower limit. Thus, the background level is assumed to be within its acceptable limits unless there is statistical evidence to the contrary. The alternative approach, which changes the burden of proof, may be used if rt is large enough.

If rt is extremely large (e.g., if $rt \geq 2{,}500$), there is probably no justification for a statistical test. Instead, the observed count rate may be compared directly to r.

Procedure B2. Determine whether the mean background count rate R_B is greater than r. Test the null hypothesis H_0: $R_B \leq r$ against the alternative hypothesis H_1: $R_B > r$.

Procedure:

1. Choose the significance level α.

2. If $N_B \leq rt$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $rt < 20$, go to Step 6. If $rt \geq 20$, go to Step 3.

3. Calculate

$$Z = \frac{0.5 + N_B - rt}{\sqrt{rt}} \tag{18.22}$$

4. Determine $z_{1-\alpha}$, the $(1-\alpha)$-quantile of the standard normal distribution (see Table G.1 in Appendix G).

5. Reject the null hypothesis if and only if $Z > z_{1-\alpha}$. Stop.

NOTE: If the background count time t is always the same, a fixed upper control limit may be calculated using the formula

$$\text{UCL} = \textbf{round}\left(rt + z_{1-\alpha}\sqrt{rt}\right)$$

where **round** denotes the function that rounds its argument to the nearest integer. Then Steps 3–5 are effectively performed by comparing the observed value N_B to UCL.

6. Determine $\chi^2_\alpha(2N_B)$, the α-quantile of the chi-square distribution with $2N_B$ degrees of freedom (see Table G.3 in Appendix G), and calculate $Q = 0.5\,\chi^2_\alpha(2N_B)$.

7. Reject the null hypothesis if and only if $Q > rt$.

EXAMPLE

Problem: To ensure adequate detection capabilities, a laboratory establishes an upper limit of 0.02 cps for beta backgrounds on a proportional counter. A 6,000-s background measurement is performed, during which 125 beta counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is greater than 0.02 cps.

Solution:	The values of the variables are $N_B = 125$, $t = 6{,}000$ and $r = 0.02$
Step 1	The significance level α is 1 - 0.95 = 0.05
Step 2	Since $N_B \geq rt = 120$ and $rt \geq 20$, go to Step 3
Step 3	Calculate $Z = (0.5 + 125 - 120) / \sqrt{120} = 0.5021$
Step 4	Table G.1 shows that $z_{0.95} = 1.645$
Step 5	Since $0.5021 \leq 1.645$, do not reject the null hypothesis. There is insufficient evidence to conclude that the beta background exceeds 0.02 cps

EXAMPLE

Problem: The same laboratory establishes an upper limit of 0.002 cps for alpha backgrounds on the same counter. A 6,000-s background measurement is performed, during which 19 alpha counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is greater than 0.002 cps.

Solution:	The values of the variables are $N_B = 19$, $t = 6{,}000$ and $r = 0.002$
Step 1	The significance level α is 1 - 0.95 = 0.05
Step 2	Since $N_B \geq rt = 12$ and $rt < 20$, go to Step 6

Step 6	Table G.3 shows that $\chi^2_{0.05}(38) = 24.88$. So, $Q = 0.5 \cdot 24.88 = 12.44$
Step 7	Since 12.44 > 12, reject the null hypothesis. The data give 95 percent confidence that the alpha background is greater than 0.002 cps.

Procedure B3. Determine whether the mean background count rate R_B is less than r. Test the null hypothesis H_0: $R_B \geq r$ against the alternative hypothesis H_1: $R_B < r$.

Procedure:

1. Choose the significance level α.

2. If $N_B \geq rt$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $rt < 20$, go to Step 6. If $rt \geq 20$, go to Step 3.

3. Calculate

$$Z = \frac{0.5 + N_B - rt}{\sqrt{rt}} \tag{18.23}$$

4. Determine $z_{1-\alpha}$, the $(1 - \alpha)$-quantile of the standard normal distribution (see Table G.1 in Appendix G).

5. Reject the null hypothesis if and only if $Z < -z_{1-\alpha}$. Stop.

   NOTE: If the background count time t is always the same, a lower control limit may be calculated using the formula

   $$\text{LCL} = \textbf{round}\left(rt - z_{1-\alpha}\sqrt{rt}\right).$$

   Steps 3–5 are then effectively performed by comparing N_B to LCL.

6. Determine $\chi^2_{1-\alpha}(2N_B + 2)$, the $(1 - \alpha)$-quantile of the chi-square distribution with $2N_B + 2$ degrees of freedom (see Table G.3), and calculate $Q = 0.5\,\chi^2_{1-\alpha}(2N_B + 2)$.

7. Reject the null hypothesis if and only if $Q < rt$.

EXAMPLE

Problem: A laboratory establishes a lower limit of 0.01 cps for beta backgrounds on a proportional counter. A 6,000-s background measurement is performed, during which 50 beta counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is less than 0.01 cps.

Solution:	The values of the variables are $N_B = 50$, $t = 6{,}000$ and $r = 0.01$
Step 1	The significance level α is $1 - 0.95 = 0.05$
Step 2	Since $N_B \leq rt = 60$ and $rt \geq 20$, go to Step 3
Step 3	Calculate $Z = (0.5 + 50 - 60) / \sqrt{60} = -1.226$
Step 4	Table G.1 shows that $z_{0.95} = 1.645$
Step 5	Since $-1.226 \geq -1.645$, do not reject the null hypothesis.

18B.3.3 Comparing the Results of Consecutive Measurements

If consecutive measurements of the background level on an instrument give significantly different values, one should be concerned about the accuracy of any laboratory sample measurements made between the two background measurements. If the background has increased, the laboratory sample activities may have been overestimated. If the background has decreased, the activities may have been underestimated. For very low background applications, when the number of observed counts per measurement approaches zero (as encountered in alpha spectrometry), the tests for comparing statistical equivalence of paired backgrounds can be confounded. In these cases, it may be better to examine populations of blanks with $N \geq 20$.

Let N_1 and N_2 denote the counts observed in two independent background measurements on the same instrument, and assume they represent Poisson distributions with unknown means. Let t_1 and t_2 denote the corresponding count times. The following two procedures may be used to determine whether the difference between the two observed values is significantly larger than would be expected on the basis of the Poisson model. Procedure B4 determines whether the second value is significantly greater than the first. Procedure B5 determines whether there is a significant difference between the two values.

Procedure B4. Determine whether the second mean background count rate R_2 is higher than the first R_1. Test the null hypothesis H_0: $R_1 \geq R_2$ against the alternative hypothesis H_1: $R_1 < R_2$.

Procedure:

1. Choose the significance level α.

2. If $N_1 / t_1 \geq N_2 / t_2$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $N_1 \geq 20$ and $N_2 \geq 20$, go to Step 3. If $N_1 < 20$ or $N_2 < 20$, go to Step 6.

3. Calculate

$$Z = \left(\frac{N_2}{t_2} - \frac{N_1}{t_1} \right) \Bigg/ \sqrt{\frac{N_1 + N_2}{t_1 t_2}} \qquad (18.24)$$

4. Determine $z_{1-\alpha}$, the $(1 - \alpha)$-quantile of the standard normal distribution.

5. Reject the null hypothesis if and only if $Z > z_{1-\alpha}$. Stop.

6. Let $p = t_1 / (t_1 + t_2)$ and $q = t_2 / (t_1 + t_2)$. If $N_1 < N_2$, calculate

$$S = \sum_{k=0}^{N_1} \binom{N_1 + N_2}{k} p^k q^{N_1 + N_2 - k} \qquad (18.25)$$

If $N_1 \geq N_2$, calculate S more efficiently using the formula

$$S = 1 - \sum_{k=N_1+1}^{N_1+N_2} \binom{N_1 + N_2}{k} p^k q^{N_1 + N_2 - k} \qquad (18.26)$$

NOTE: For any nonnegative integers n and k, the notation $\binom{n}{k}$ denotes a *binomial coefficient*, usually read "n choose k," which is the number of possible combinations of n objects chosen k at a time. For example, $\binom{4}{1} = 4$, $\binom{4}{2} = 6$, $\binom{4}{3} = 4$, and $\binom{4}{4} = 1$. In general, for $0 \leq k \leq n$, the value of $\binom{n}{k}$ equals $\frac{n!}{k!(n-k)!}$, where the symbol ! denotes the "factorial" operator. The number of combinations of n objects chosen k at a time is also denoted sometimes by ${}_nC_k$.

7. Reject the null hypothesis if and only if $S \leq \alpha$.

EXAMPLE

Problem: A 60,000-s background measurement is performed on an alpha spectrometer and 15 total counts are observed in a particular region of interest. After a test source is counted, a 6,000-s background measurement is performed and 3 counts are observed. Assuming Poisson counting statistics, is the second measured count rate (0.0005 cps) significantly higher than the first (0.00025 cps) at the 5 percent significance level?

Solution: The variables are $N_1 = 15$, $t_1 = 60{,}000$, $N_2 = 3$, and $t_2 = 6{,}000$

Step 1 The significance level α is specified to be 0.05

Step 2 Since $N_1 / t_1 = 0.00025 < 0.0005 = N_2 / t_2$, $N_1 < 20$, and $N_2 < 20$, go to Step 6

Step 6 $p = \frac{60{,}000}{66{,}000} = \frac{10}{11}$ and $q = \frac{6{,}000}{66{,}000} = \frac{1}{11}$. Since $N_1 \geq N_2$, calculate S using the second formula.

$$S = 1 - \left(\binom{18}{16} \left(\frac{10}{11}\right)^{16} \left(\frac{1}{11}\right)^{2} + \binom{18}{17} \left(\frac{10}{11}\right)^{17} \left(\frac{1}{11}\right)^{1} + \binom{18}{18} \left(\frac{10}{11}\right)^{18} \left(\frac{1}{11}\right)^{0} \right)$$

$$= 1 - 0.7788 = 0.2212 .$$

Step 7 Since $S \geq \alpha$, there is not enough evidence to reject the null hypothesis. The second measured count rate is not significantly higher than the first.

Procedure B5. Determine whether the mean background count rates are different. Test the null hypothesis H_0: $R_1 = R_2$ against the alternative hypothesis H_1: $R_1 \neq R_2$.

Procedure:

1. Choose the significance level α.
2. If $N_1 / t_1 = N_2 / t_2$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $N_1 < 20$ or $N_2 < 20$, go to Step 6. If $N_1 \geq 20$ and $N_2 \geq 20$, go to Step 3.
3. Calculate Z using Equation 18.24.
4. Determine $z_{1-\alpha/2}$, the $(1 - \alpha / 2)$-quantile of the standard normal distribution.
5. Reject the null hypothesis if and only if $|Z| > z_{1-\alpha/2}$. Stop.

6. If $N_1 / t_1 < N_2 / t_2$, use Procedure B4 with significance level $\alpha / 2$ to determine whether $R_1 < R_2$. If $N_1 / t_1 > N_2 / t_2$, use Procedure B4 with significance level $\alpha / 2$ and with the observations reversed to determine whether $R_2 < R_1$.

18B.4 Negative Activities

When the measured count rate for a test source is less than that of the corresponding instrument background, giving a negative value for the source activity, Procedure B4 may be used to determine whether the difference between the two count rates is significantly more than should be expected on the basis of the Poisson model and the assumption that the source is a blank. (Let N_1 and t_1 be the source count and counting time and let N_2 and t_2 be the background count and counting time.). If a significant difference is found, it may indicate that the background measurement was biased, the true background is variable or non-Poisson, or the instrument is unstable. As background counts approach zero, the assumption of Poisson statistics begins to fail. This mean-centered approach may lead the analyst to an inappropriate conclusion. In these cases, an examination of a larger population of blanks is more appropriate.

18B.5 References

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